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LABORATORY EVALUATION OF THE HACH DR-EL DIRECT READING, PORTABLE ENGINEERS' LABORATORY

W. S. Midkiff, et al

New Mexico State University
University Park, New Mexico

April 1972

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LABORATORY EVALUATION OF THE HACH DR-EL, "DIRECT READING," PORTABLE ENGINEERS' LABORATORY

INTRODUCTION

The Hach DR-EL was originally designed to provide a convenient, accurate means of testing water in the field. Techniques of performing standard wet chemical analyses have been simplified with a minimum sacrifice in accuracy. In the many instances, this slight sacrifice in accuracy is more than offset by the fact that a test can be performed at the sampling site, before physical, biological, or chemical changes in the sample occur.

Apparently, the simplified techniques for analysis are quite attractive. The Hach DR-EL has been observed in a number of wastewater treatment plant laboratories about the state where they are presumably being used for routine laboratory analyses. Certainly, the ease with which tests may be performed is an advantage to any technician. The Hach DR-EL, will be an excellent contribution to wastewater treatment plant laboratories if its presence encourages performance of routine monitoring of water quality.

How much accuracy and precision has been sacrificed in an effort to simplify procedure? Is this unit acceptable for field testing, and further, is it acceptable for routine laboratory analyses? The direct reading aspect of the unit, with no suggestion that calibration of the instrument may be inexact or vary with time, is in itself cause to examine the precision and accuracy obtainable. Calibration with standard solutions has always been the basis of a credible study.

In a special problems summer course, graduate students in Sanitary Engineering at New Mexico State University have evaluated the accuracy and precision of tests performed with the Hach DR-EL.

DISCUSSION

The tests included in the Hach DR-EL kit were predominately colorimetric and titrimetric. Replicate analyses were conducted on standard solutions to determine precision or repeatability of the tests and to determine accuracy. The fact that a test is repeatable gives no assurance that the value being repeated is the accurate or correct one.

Most of the colorimetric tests follow Beer's Law. That is, water containing the mineral in question is mixed with a reagent to cause a color development. The intensity of color is proportional to the concentration of the mineral in solution. More exactly, the logarithm of percent transmittance is inversely proportional to the concentration. A Bausch and Lomb 505 Spectrophotometer was used to determine the wavelengths characteristic of the colorimetric tests.

The relative amplitude of the specific wavelengths absorbed by the color associated with each of the various colorimetric tests is shown on a recording made with the "505". On the same recording is shown the relative amplitude of the specific wavelengths transmitted by the color filter provided with the Hach DR-EL for that particular test. This recording was made by placing the filter in the "505" in the same manner as a water sample. Ideally, the wavelength of maximum transmittance through the filter should be the same as the wavelength of maximum absorption by the sample and reagent.

A simple DC battery powered filter colorimeter is included in the Hach kit. Its precision (not accuracy) was compared to a commonly used laboratory colorimeter, the Bausch and Lomb Spectronic 20. The performance of the Spectronic 20 is widely accepted as adequate for routine laboratory

analyses. Colorimetric test were run with the Spectronic 20 on the same samples previously analyzed on the Hach colorimeter. The wavelength was selected to be that of maximum absorption as indicated on the Bausch and Lomb 505. If a scan revealed no absorption peak, the wavelength selected was the same as the Hach filter. Plots of concentration vs. percent transmittance were made for the replicate analyses. These were compared with the DR scales by converting the direct readout values to percent transmittance. No attempt was made to zero the DR scale with standard solutions.

When performing a titrimetric test a titrant of known concentration is introduced into a measured quantity of sample until an indication (usually a color change) is given that the sample has reacted completely with the titrant. At this point, the number of equivalents of titrant added are equal to the number of equivalents of sample. By knowing how much titrant was used, the normality of the sample can be calculated. (Volume of titrant x normality of titrant = volume of sample x normality of sample).

Errors in the titrimetric analyses could be caused by inexact normality of the titrant or by errors in volumetric measurements. The normality of the titrants were standardized by titrating them against solutions of measured volume and predetermined normality (using gravimetric techniques). The volumetric measures in the Hach kit, droppers, pipets, etc., were calibrated gravimetrically using Class A, volumetric transfer pipets as standards. The chemical contained in plastic pillows should all be in excess and their exact quantities are therefore not critical.

The recommended procedure for titration with the Hach DR-EL is to use the bulb buret in the stand provided so that delivery of titrant can be

precisely read. To insure that all of the titrant reaches the sample, the titrant is normally added dropwise rather than trickled down the side of the beaker. This being the case, the investigators chose to deviate from recommended procedure and evaluate the performance obtained using the bulb buret free hand, without the support provided. The delivery of each bulb buret was carefully calibrated for drops per ml with its respective titrant. The investigators wanted to determine if the speed and simplicity of this technique justified the anticipated loss in precision and accuracy.

CONCLUSIONS

In general, the colorimetric analyses were quite precise. Precision of the Hach colorimeter tested exceeded that of the Spectronic 20 reference. The accuracy of the DR scales was better for some tests than others, but could be improved by adjusting the direct readout scale to coincide with a known standard approximately mid-range on the scale, or near the value to be measured. Zeroing the DR scale with a blank in some cases caused the DR scale to be shifted considerably from the actual values.

Attention should be given to the variation between replicates. These data were the results of conscientious graduate students. The fact that scatter is great in some instances should be a reminder to technicians that colorimetric tests are not exact. The technician is advised to determine for himself what type of repeatability he can expect.

The investigators recommend the DR scale for each test be verified against standard solutions. If the accuracy is not acceptable, the transmittance scale should be used instead and a calibration curve of percent transmittance vs. known concentration of standard solutions should be prepared by the technician.

The accuracy of the titrimetric tests was excellent for most purposes. The normalities of the titrant were found to be within $\pm$ 2.5% of their nominal values. Each dropper was calibrated with the specific solution it was to deliver and the number of drops per ml were determined within $\pm$ 1 drop/ml. Error from pipets was insignificant. Precision was dependent primarily on operator care in measuring sample size. In some cases larger samples would improve the precision of the test. The numerical error is approximately the same for a 50 ml sample as a 10 ml sample,

but the percentage error is much less. The end point on some color titrations was more difficult to distinguish at high concentrations. In these cases, the sample should be diluted to a range where the end point is better defined.

Fairly precise and accurate titrations can be performed if the dropper is used as a buret. When mounted in its stand, increments of less than a single drop can be read. Nonetheless, whole, single drops are normally delivered. Improved precision could be obtained if the tip of the droppers was designed to deliver smaller drops.

Experimental results indicated that the freehand technique of titration was rapid and could be justified. However, variation in drop size hinders the accuracy of this technique. The meniscus reading should be used rather than the number of drops to indicate volume of titrant.

APPENDIX I

SUGGESTED HARDWARE MODIFICATIONS

SUGGESTED HARDWARE MODIFICATIONS

A complete series of tests requires approximately three hours. This time could be shortened considerably by including a second set of colorimeter bottles in the kit. This would enable an experienced operator to run two or three samples concurrently. Additional bottles should be selected for variation in transmittance of less than 1.0%.

As an aid to mixing, polyethylene stoppers should be included. Shaking is much more effective than swirling.

The test for dissolved oxygen is quite difficult to conduct due to air being trapped by the flat bottom of the glass stopper. A tapered-bottomed stopper should be substituted. Hach can provide at additional cost, a 60 ml bottle with a tapered stopper.

Drops from the droppers are larger than those from a buret. This means that the end point cannot be determined as closely with the dropper furnished as with a buret. The precision of these titrations can be improved by using larger sample volumes. Another alternative is to provide droppers of different tip design which would deliver a smaller drop.

The DR scale for the phosphate test is calibrated in terms of the PO_4^{3-} species even though a negligible portion of total phosphorus concentration is actually present as PO_4^{3-}. It is suggested that the DR scale furnished should be calibrated in terms of P.

Plastic or metal DR scales would be more useful for the colorimetric tests, as the present cards are easily bent and dog-eared with frequent use of the kit. However, Hach reports that metal scales are subject to bending and the plastic scales, which are currently available, develop a static charge which inhibits the free movement of the meter needle. Closer tolerance

between the card and the slot would reduce variations in position from run-to-run. In addition, the pages of the instruction manual should also be sprayed with a transparent plastic coating to protect against spills of chemicals.

A timer with an alarm is a very useful addition to the kit. Some of the color developments are time dependent.

The wide range color indicator solution should be packaged in a bottle similar to that used for phenolphthalein, thereby eliminating the need to dirty the pipet.

APPENDIX II

GRAPHICAL RESULTS

The following pages consist of calibration charts and discussions of each test included in the Hach DR-EL.

ALKALINITY TEST

The alkalinity test is titrimetric. The alkalinity, predominately carbonate and bicarbonate, is titrated with a standard acid, usually 0.02 N H_2SO_4, to end points of approximately pH 8.4 and pH 4.6. Color indicators, phenolphthalein and bromocresol green - methyl red, are used respectively. A Coleman Model 10 pH meter, calibrated against certified buffer solutions of known pH values, was used to monitor the titration and to evaluate the titer and color indicators. The acid was standardized by titrating a 10 ml solution of 0.02 N sodium carbonate, Na_2CO_3.

Only drop counting techniques has been evaluated. This technique is not recommended by Hach. They suggest using the dropper as a buret in the stand provided.

Standards

Stock solution of 0.02 N (1000 mg/l as $CaCO_3$) sodium carbonate was made by dissolving 1059.9 mg Na_2CO_3 in distilled water and diluting to 1.0 liter. The following standards were then made by diluting the stock solution.

1	1000 mg/l as $CaCO_3$
2	500 mg/l as $CaCO_3$
3	250 mg/l as $CaCO_3$
4	100 mg/l as $CaCO_3$

Calibrations

10 ml pipet	5 replicates	9.953 $\pm$ 0.0098 ml
2.5 ml dropper	16 $\pm$ 1 drops per ml	
Standardized titer	0.01961 N H_2SO_4	

Conclusions

Variation between replicates was approximately 5%. When a 10 ml sample is being titrated, one drop is approximately equivalent to 6 mg/l alkalinity as $CaCO_3$. If greater precision is required a 20 ml sample can be titrated. In this case, one drop is approximately equivalent to 3 mg/l alkalinity as $CaCO_3$.

The dropper must be held vertically to insure uniform drop size.

Color indicator endpoints should be verified during a sample titration using a pH meter. Methyl orange could be used in place of bromocresol green-methyl red indicator.

The technician is advised to practice with standards until he can get the indicated value and the actual value to coincide.

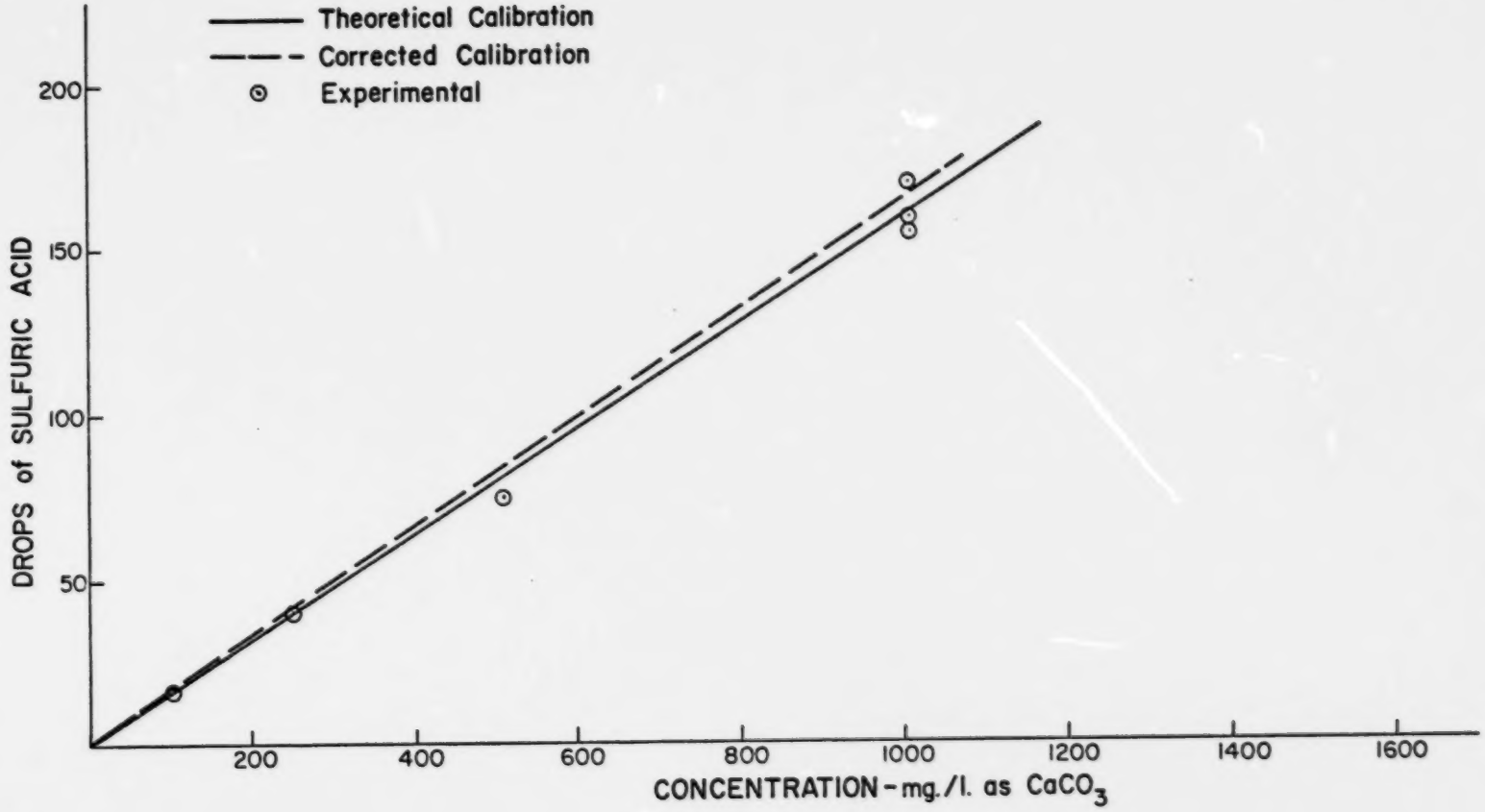

Figure 1. ALKALINITY, TOTAL and PHENOLPHTHALEIN

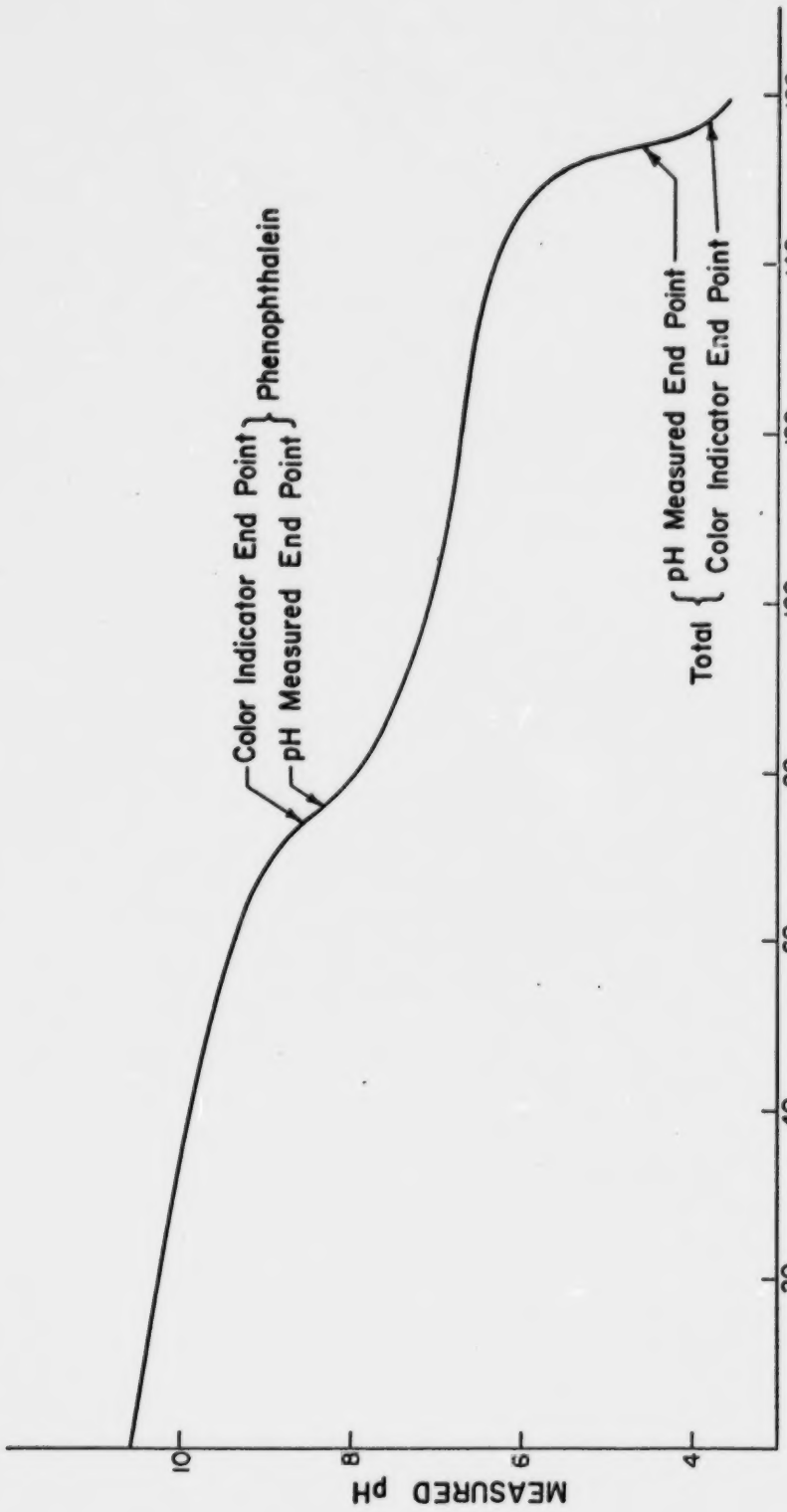

Figure 2. ALKALINITY TITRATION

CHLORIDE TEST

The chloride test is titrimetric. This test consists of titrating with mercuric nitrate in the presence of a diphenylcarbazone indicator-buffer. The end point, conversion of all of the chloride to mercuric chloride, is apparent as a color change from light yellow to pale pinkish purple. The color change is sharp for low concentrations but is gradual for higher concentrations.

Only the drop counting technique has been evaluated. This technique is not recommended by Hach. They suggest using the dropper as a buret in the stand provided.

Standards

A stock solution of 640 mg/l as chloride was made by dissolving 1.3459 grams of potassium chloride in distilled water and diluting to 1.0 liter. The following standards were made by diluting the stock solution.

1	320 mg/l as Cl^-
2	160 mg/l as Cl^-
3	80 mg/l as Cl^-
4	40 mg/l as Cl^-
5	20 mg/l as Cl^-
6	10 mg/l as Cl^-

Calibrations

10 ml pipet	5 replicates	9.953 ± 0.0098 ml
2.5 ml dropper	17 ± 1 drops per ml	

Conclusions

Variation between replicates was approximately 6%. When a 10 ml sample is being titrated, one drop is approximately equivalent to 3 mg/l as Cl^-. If greater precision is required, a larger sample may be titrated.

The dropper must be held vertically to insure uniform drop size.

The technician is advised to practice with standards until he can get the indicated value and the actual value to coincide.

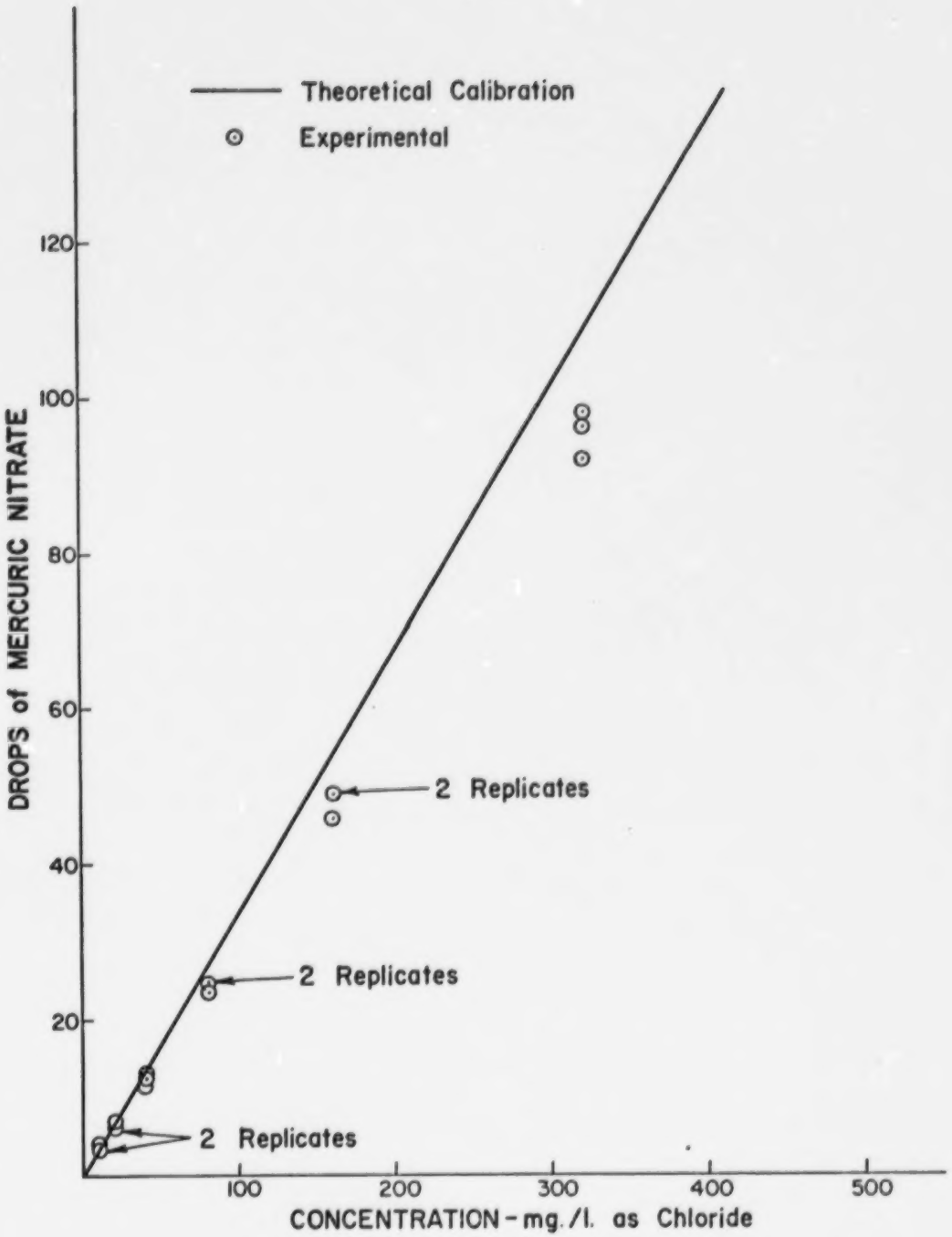

Figure 3. CHLORIDE

CHROMIUM TEST

The chromium test is colorimetric. Diphenylcarbohydrazide reacts with hexavalent chromium to form a red-purple color.

Standards

A stock solution of 100 mg/l as chromium was made by dissolving 0.3735 g of potassium chromate, K_2CrO_4, in distilled water and diluting to 1.0 liter. The following standards were made by diluting the stock solution.

1	0.1 mg/l as Cr^{6+}
2	0.2 mg/l as Cr^{6+}
3	0.4 mg/l as Cr^{6+}
4	0.8 mg/l as Cr^{6+}
5	1.2 mg/l as Cr^{6+}

Calibrations

25 ml graduated cylinder	3 replicates	24.81 ± 0.136 ml

Conclusions

Variation between replicates is less than 0.002 mg/l at chromium concentrations of 0.1 mg/l and is less than 0.05 mg/l at chromium concentrations of 1.2 mg/l. This precision of approximately 4 percent is acceptable for most routine analyses.

The D-R scale was quite accurate with this test. It is recommended, however, that the technician calibrate his instrument or verify calibration with standard solutions.

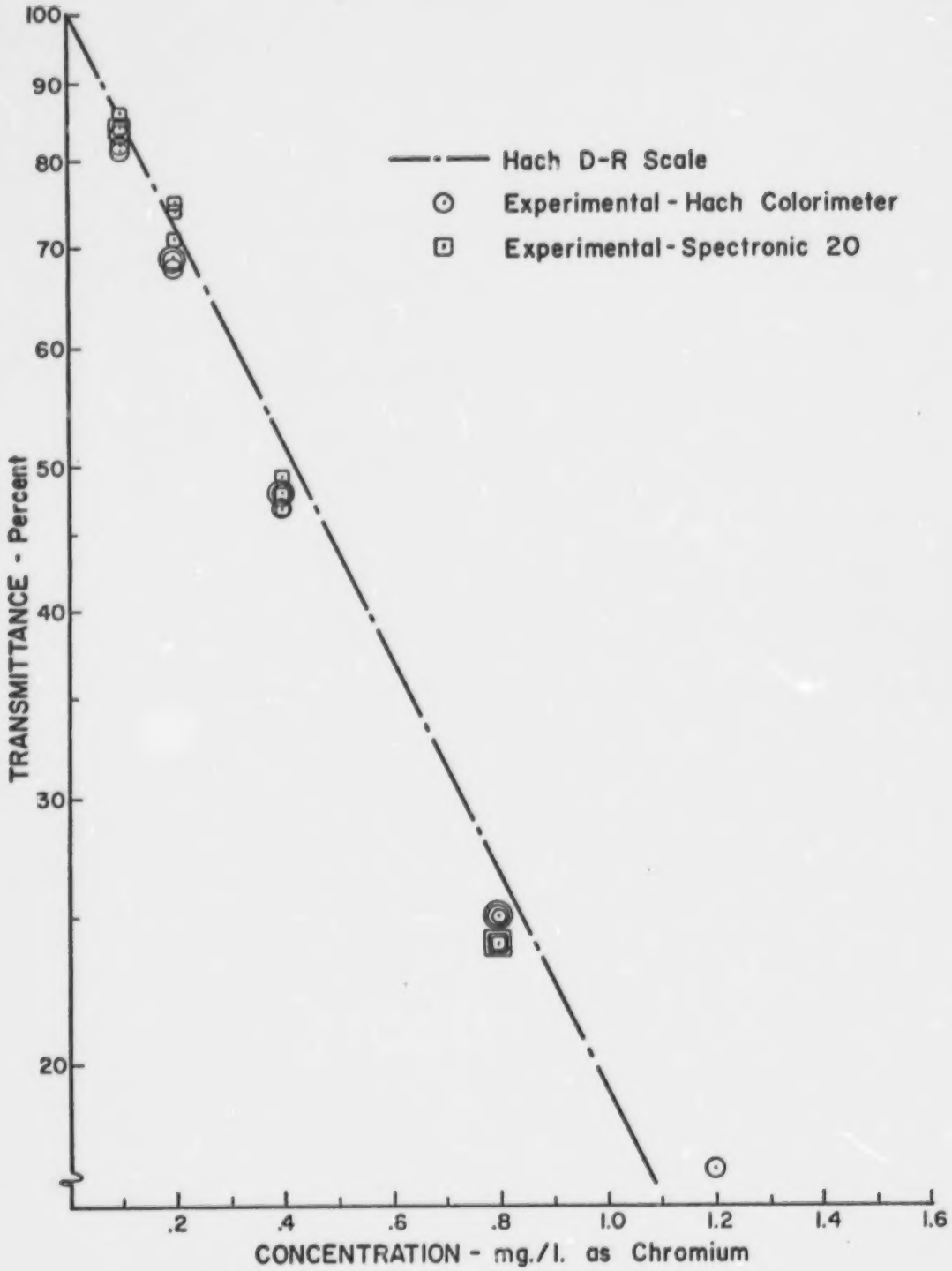

Figure 4. CHROMIUM

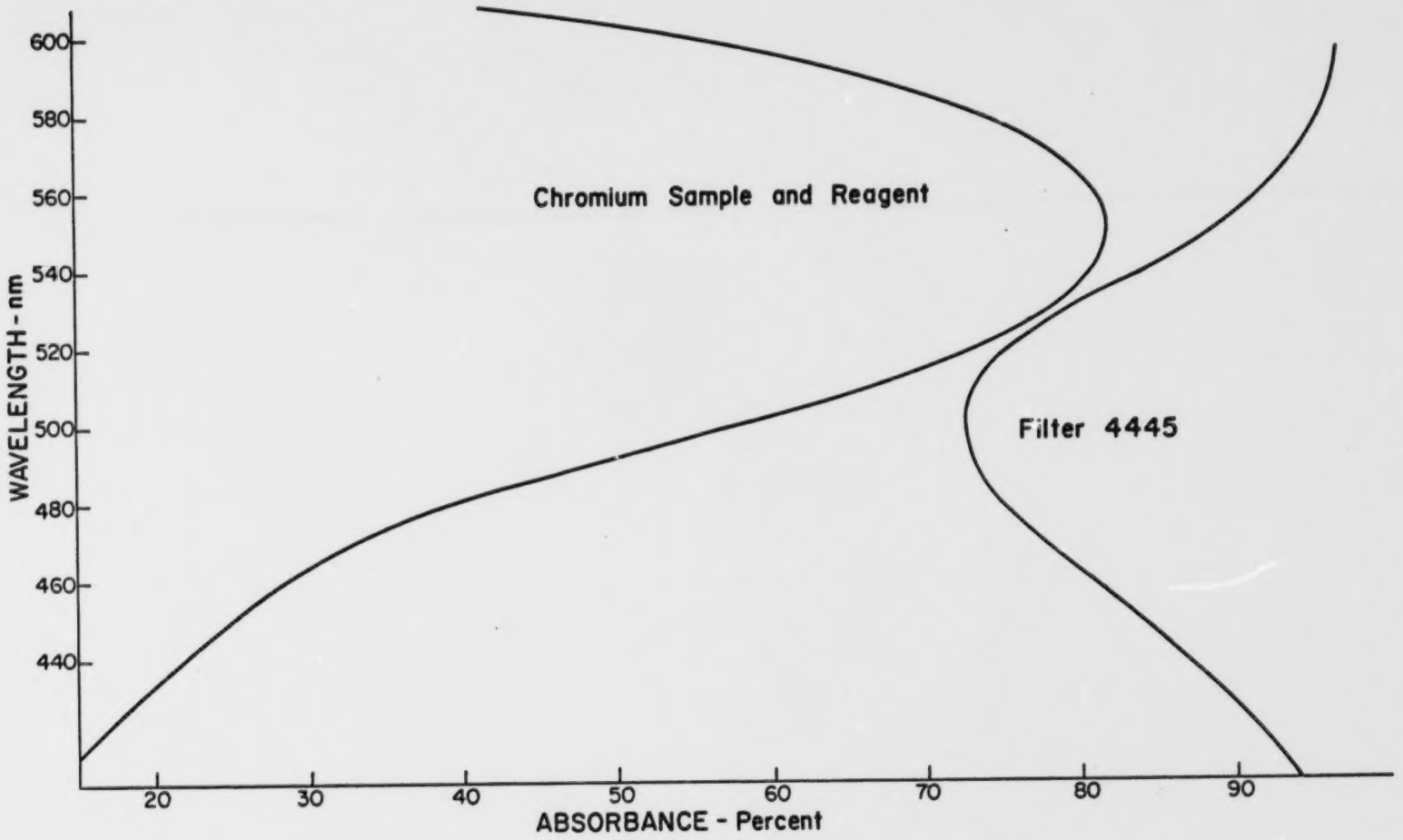

Figure 5. CHROMIUM ABSORBANCE SPECTRUM

COPPER TEST

The copper test is colorimetric. Cupric ions form a yellow colored chelate with cuprethol.

Standards

A stock solution of 1000 mg/l as Cu^{2+} was made by dissolving 2.52 g of copper sulfate, $CuSO_4$, in distilled water and diluting to 1.0 liter. A second stock solution of 100 mg/l was made by diluting 100 ml of the first stock of 1.0 liter. The following standards were made by diluting the second stock solution.

1	0.5 mg/l as Cu^{2+}
2	1.0 mg/l as Cu^{2+}
3	1.5 mg/l as Cu^{2+}
4	2.0 mg/l as Cu^{2+}

Calibrations

25 ml graduated cylinder	3 replicates	24.81 ± 0.134 ml

Conclusions

Variation between replicates is less than 0.2 mg/l. This precision is acceptable for most routine monitoring.

The accuracy of the D-R scale provided for this test was not acceptable. It is recommended that the technician check the calibration of his instrument with standard solutions. If unacceptable, the technician should prepare his own calibration chart using the transmittance scale and standard solutions.

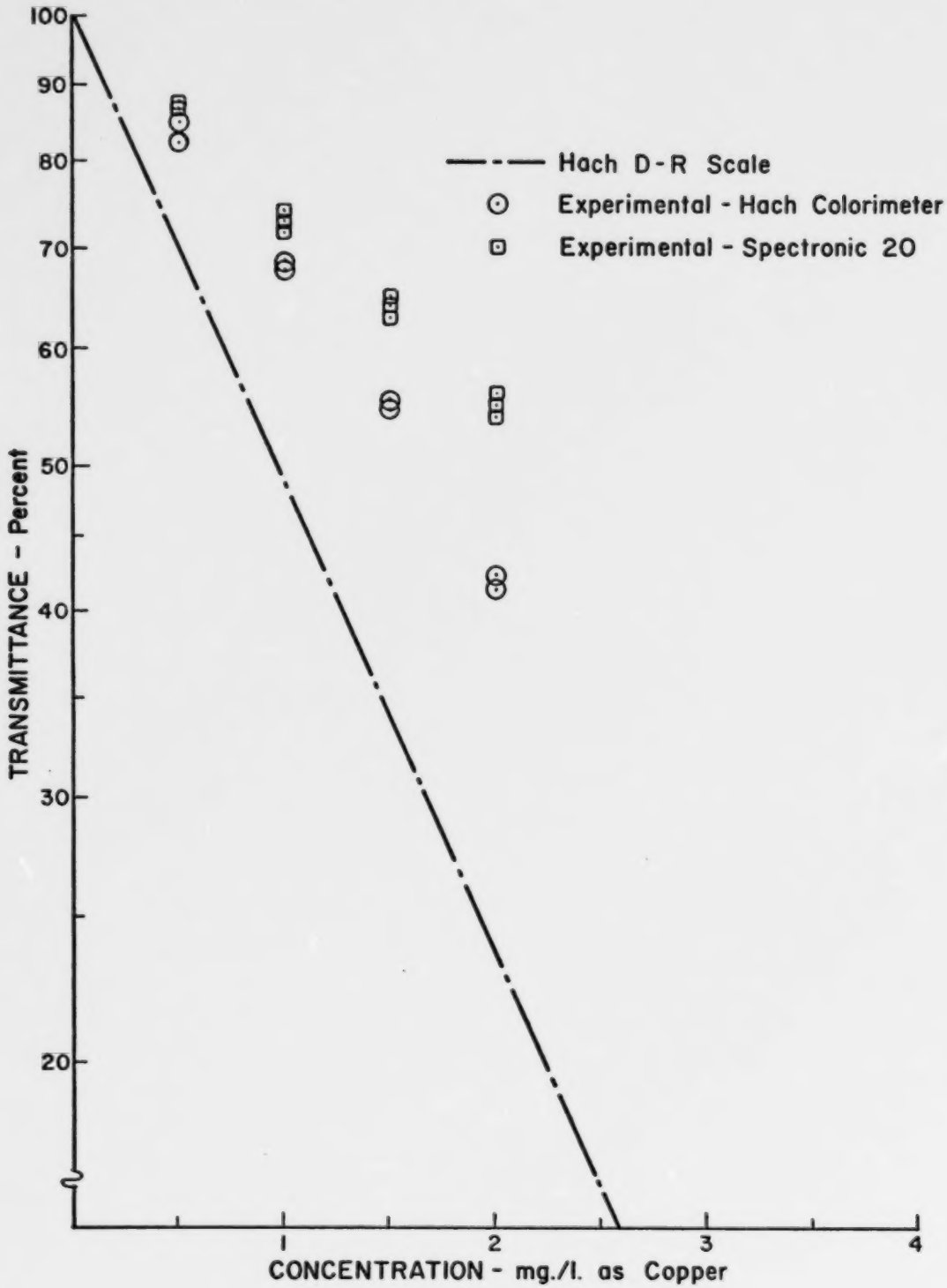

Figure 6. COPPER

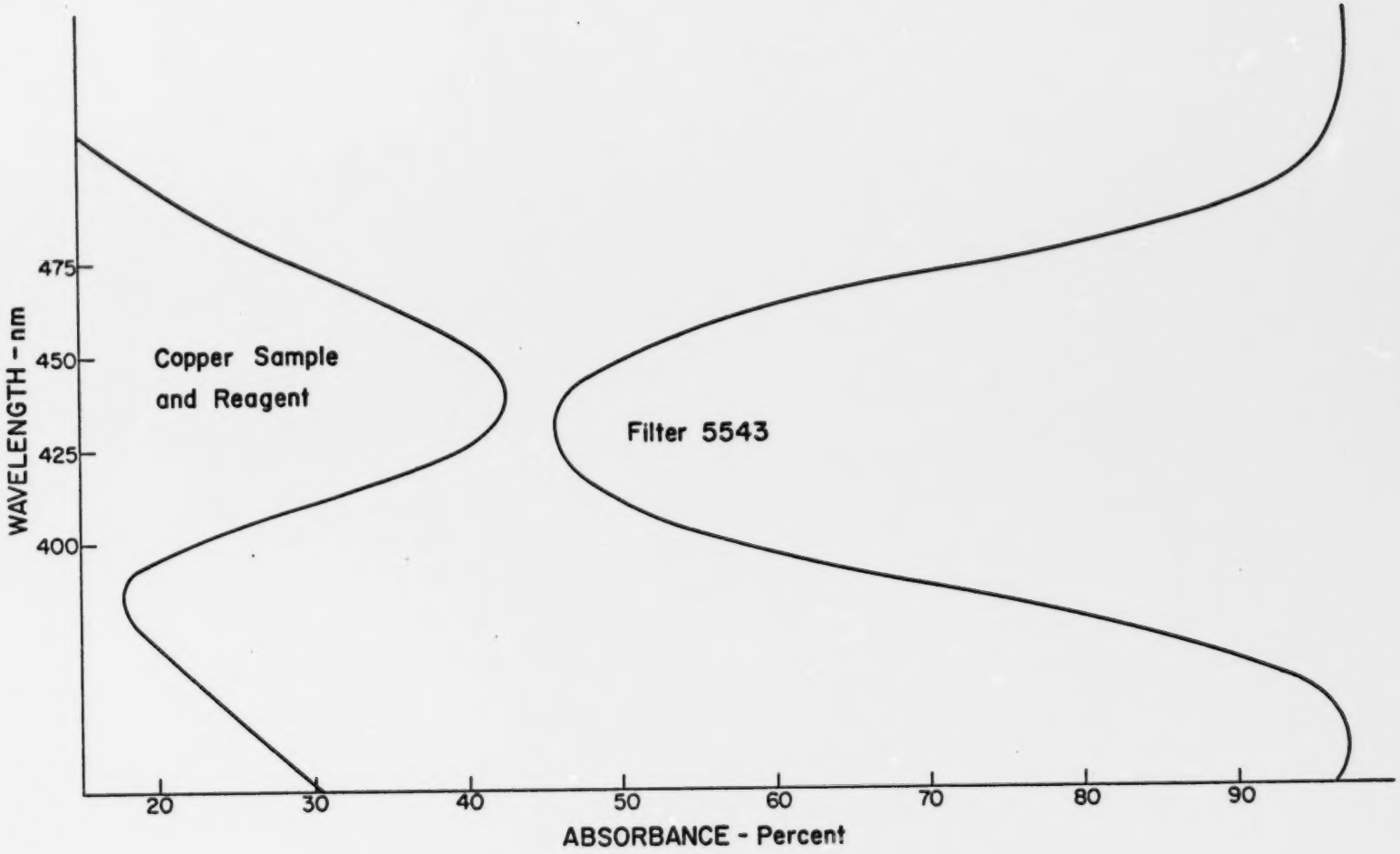

Figure 7. COPPER ABSORBANCE SPECTRUM

FLUORIDE TEST

The fluoride test is colorimetric. An initial volume of SPADNS fluoride reagent reacts with fluoride ion to cause a decrease in initial intensity. Beer's Law is not followed. The D-R scale for this test was equivalent to 32% transmittance at 0 mg/l concentration and 100% transmittance at 2 mg/l. The Hach colorimeter was zeroed on 32% using a distilled water blank with 5.0 ml fluoride reagent dissolved in it. A 2 mg/l standard was prepared to calibrate the meter at 100% transmittance. The temperature of the standards was maintained at 21° C with a water bath.

Standards

A stock solution of 100 mg/l F was made by dissolving 221 mg of NaF in distilled water and diluting to 1.0 liter. The following standards were made by diluting the stock solution.

1	.25 mg/l as F^-
2	.50 mg/l as F^-
3	1.00 mg/l as F^-
4	1.50 mg/l as F^-

Calibrations

10 ml pipet	5 replicates	9.953 ± 0.0098 ml

Conclusions

Variation between replicates was less than 0.20 mg/l. This precision is acceptable for field use or coarse monitoring.

The D-R scale for this test has adequate accuracy if it is adjusted to a standard solution in the range of expected use.

Greater accuracy is obtained when the standards and samples are kept at 20° C $\pm$ 1° C.

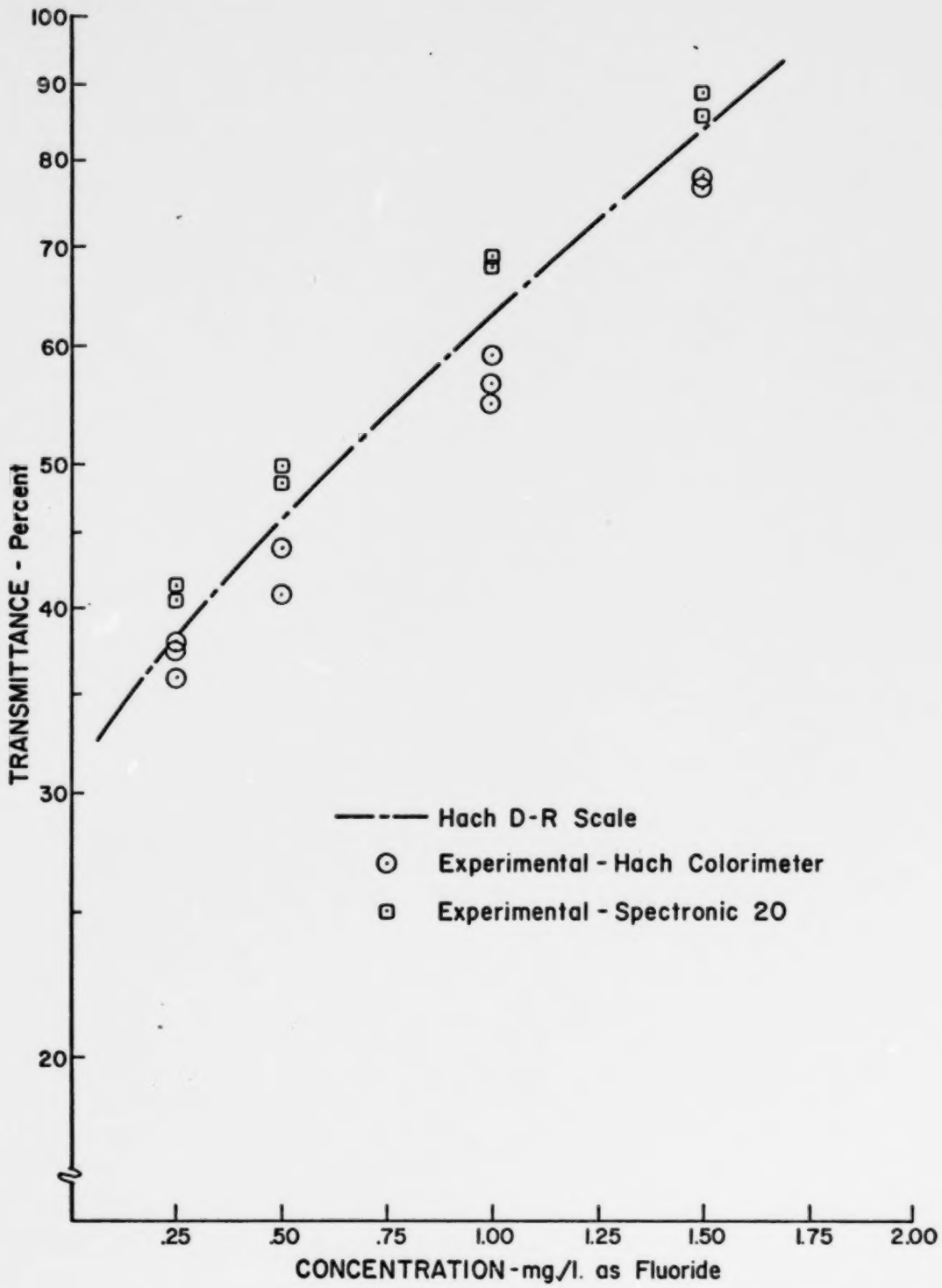

Figure 8. FLUORIDE TEST

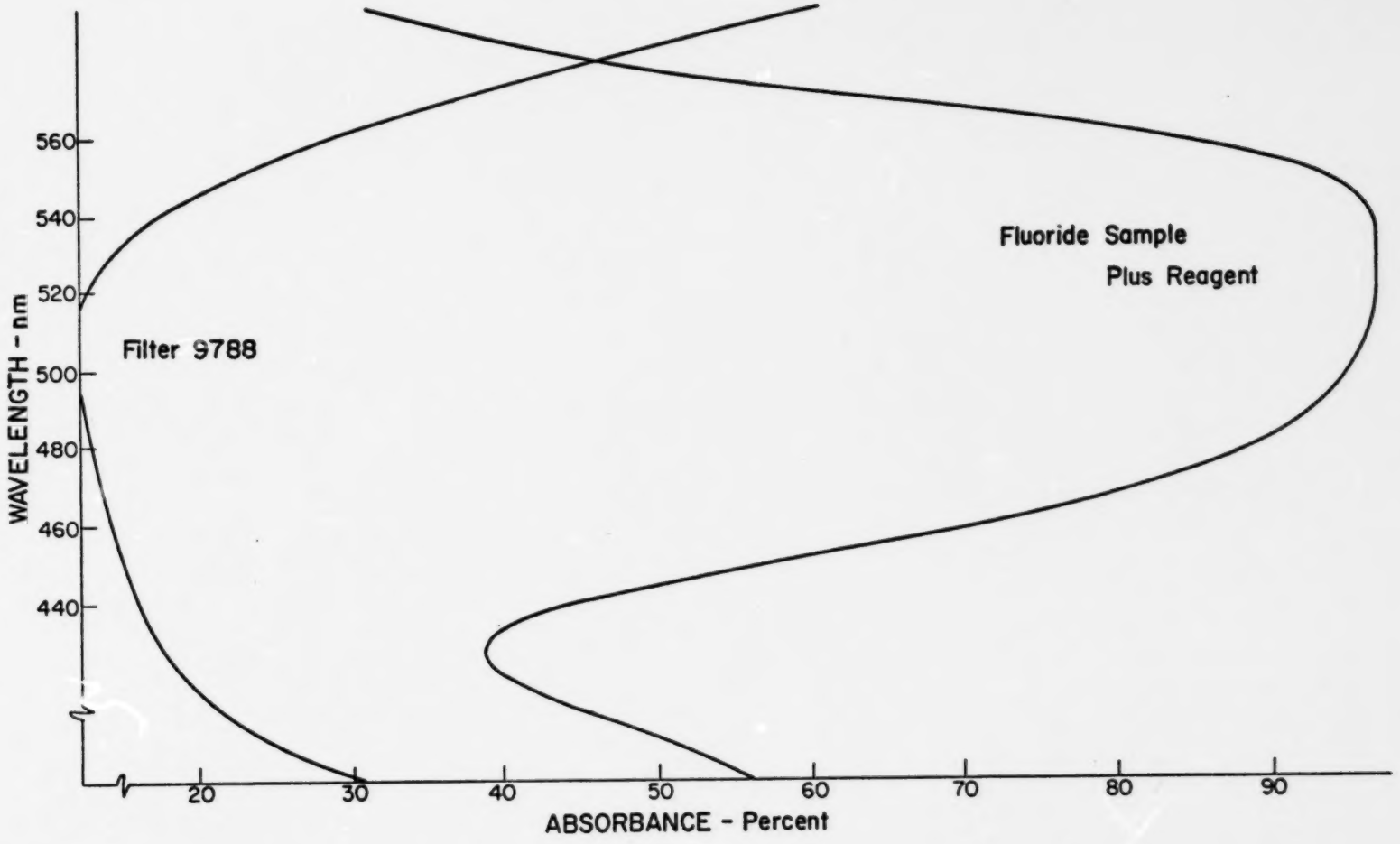

Figure 9. FLUORIDE ABSORBANCE SPECTRUM

HARDNESS (CALCIUM) TEST

The calcium hardness test is titrimetric. Potassium hydroxide is added to precipitate the magnesium present. The titrant EDTA is used in the presence of a color indicator. EDTA forms a complex with the divalent calcium ions until excess EDTA remains to free the color indicator.

Only the drop counting technique has been evaluated. This technique is not recommended by Hach. They suggest using the dropper as a buret in the stand provided.

Standards

A stock solution of 400 mg/l calcium as $CaCO_3$ was made by dissolving 588 mg $CaCl_2 \cdot 2H_2O$ in distilled water and diluting to 1.0 liter. The following standards were made by diluting the stock solution.

1	400 mg/l Ca^{2+} as $CaCO_3$
2	200 mg/l Ca^{2+} as $CaCO_3$
3	100 mg/l Ca^{2+} as $CaCO_3$
4	50 mg/l Ca^{2+} as $CaCO_3$

Calibrations

10 ml pipet	5 replicates	9.953 $\pm$ 0.0098 ml
2.5 ml dropper	12 $\pm$ 1 drops per ml	
Standardized titer	0.0204 N EDTA	

Conclusions

Variation between replicates was approximately 4%. When a 10 ml sample is being titrated, one drop is approximately equivalent to 8.5 mg/l calcium as $CaCO_3$. If greater precision is required, a 20 ml sample can be titrated.

In this case, one drop is approximately equivalent to 4.25 mg/l calcium as $CaCO_3$. The error in accuracy results from the difficulty in determining the quantity of titrant in each drop.

The dropper must be held vertically to insure uniform drop size.

The best results were obtained when the titrant was added by the drop until the first blue color appeared.

The technician is advised to practice with standards until he can get the indicated value and the actual value to coincide.

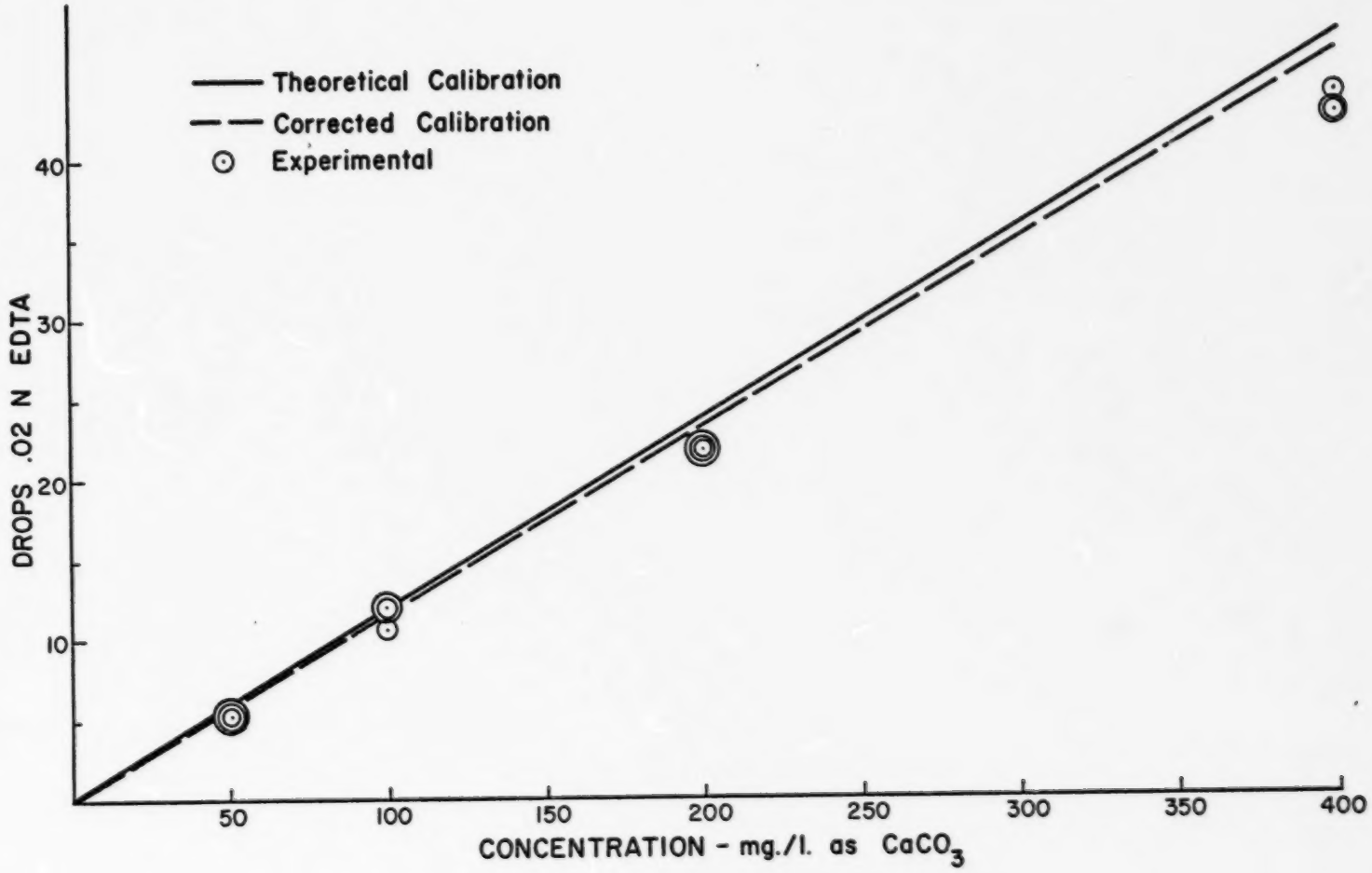

Figure 10. CALCIUM HARDNESS TEST

HARDNESS (TOTAL) TEST

The total hardness test is titrimetric. The titrant EDTA is used in the presence of a color indicator. EDTA forms a complex with the multivalent hardness ions until excess EDTA remains to free the color indicator. This test measures both calcium and magnesium. Magnesium hardness is found by subtracting the calcium hardness from the total hardness.

Only the drop counting technique has been evaluated. This technique is not recommended by Hach. They suggest using the dropper as a buret in the stand provided.

Standards

Standards containing only magnesium were used for these tests. A stock solution of 40 mg/l magnesium as $CaCO_3$ was made by dissolving 91.2 mg $MgCl_2 \cdot 6H_2O$ in distilled water and diluting to 1.0 liter. The following standards were made by diluting the stock solution.

1	40 mg/l as $CaCO_3$
2	20 mg/l as $CaCO_3$
3	10 mg/l as $CaCO_3$
4	5 mg/l as $CaCO_3$

Calibrations

10 ml pipet	5 replicates	9.953 ± 0.0098 ml
2.5 ml dropper	12 ± 1 drops per ml	
standardized titer	0.0204 N EDTA	

Conclusions

There was no variation between three replicates at four different concentrations. When a 10 ml sample is being titrated, one drop is approximately

equal to 8.5 mg/l hardness as $CaCO_3$. If greater precision is required, a 20 ml sample can be titrated. In this case, one drop is approximately equivalent to 4.25 mg/l hardness as $CaCO_3$.

An error in accuracy results from the difficulty in determining the quantity of titrant in each drop.

The non-linear array of calibration points on this test suggests that the quality of the standard solutions was suspect.

The dropper must be held vertically to insure uniform drop size.

The best results were obtained for this test when the titrant was added by the drop until the first true color change occurred.

The technician is advised to practice with the standard solution until he can get the indicated value and the actual value to coincide.

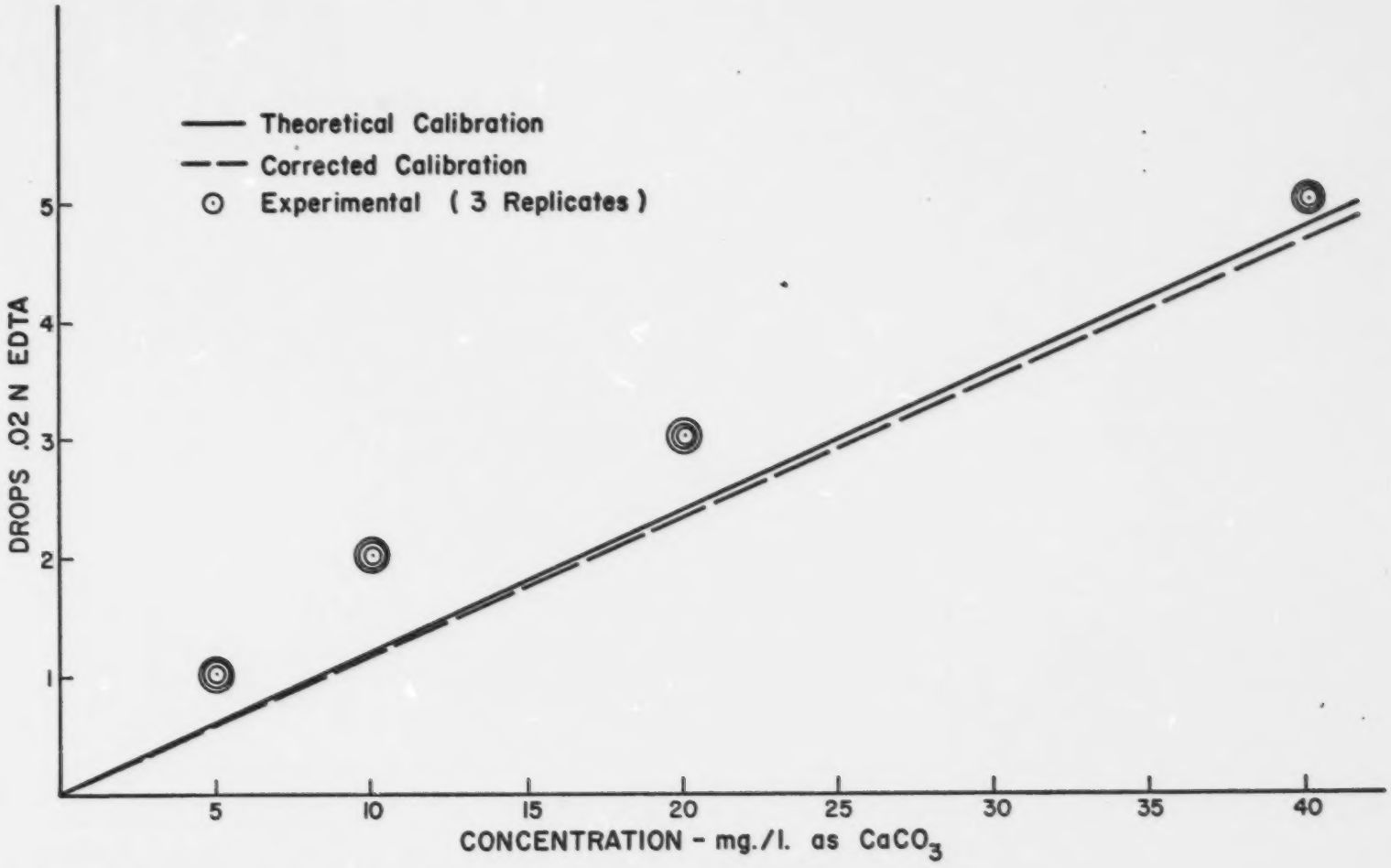

Figure II. TOTAL HARDNESS TEST

IRON TEST

The iron test is colorimetric. 1,10 - phenanthroline combines with iron to form an orange color.

Standards

A stock solution containing 200 mg/l Fe was made by dissolving 1.404 grams ferrous ammonium sulfate into a solution of 20 concentrated H_2SO_4 and 50 ml distilled water. 0.1 N $KMnO_4$ was then added dropwise until a faint pink color persisted. This solution was then diluted to 1.0 liter with distilled water.

This solution was further diluted to give the following standards.

1	0.5 mg/l Fe^{2+}
2	1.0 mg/l Fe^{2+}
3	1.5 mg/l Fe^{2+}
4	2.0 mg/l Fe^{2+}

Calibrations

10 ml pipet	5 replicates	9.953 ± 0.0098 ml

Conclusions

Variation between replicates was less than 0.025 mg/l or approximately 5 percent. This precision is acceptable for field use and routine laboratory analyses.

It is recommended that the technician calibrate or verify calibration of the D-R scale with standard solutions. The D-R scale for this test, when adjusted to a standard solution in the range of expected use should provide acceptable accuracy. If not, the technician should prepare his own calibration chart using the transmittance scale and standard solutions.

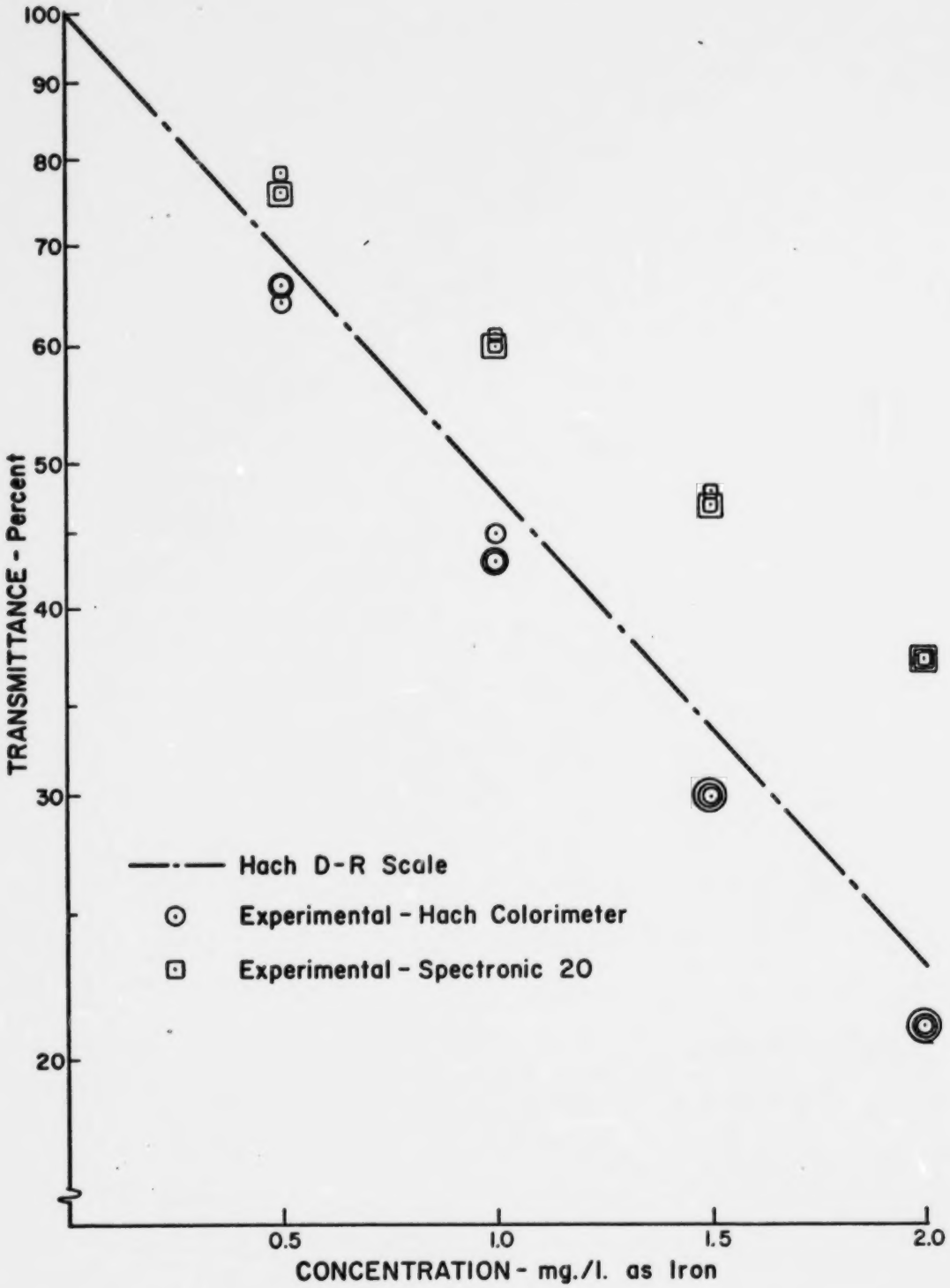

Figure 12. IRON TEST

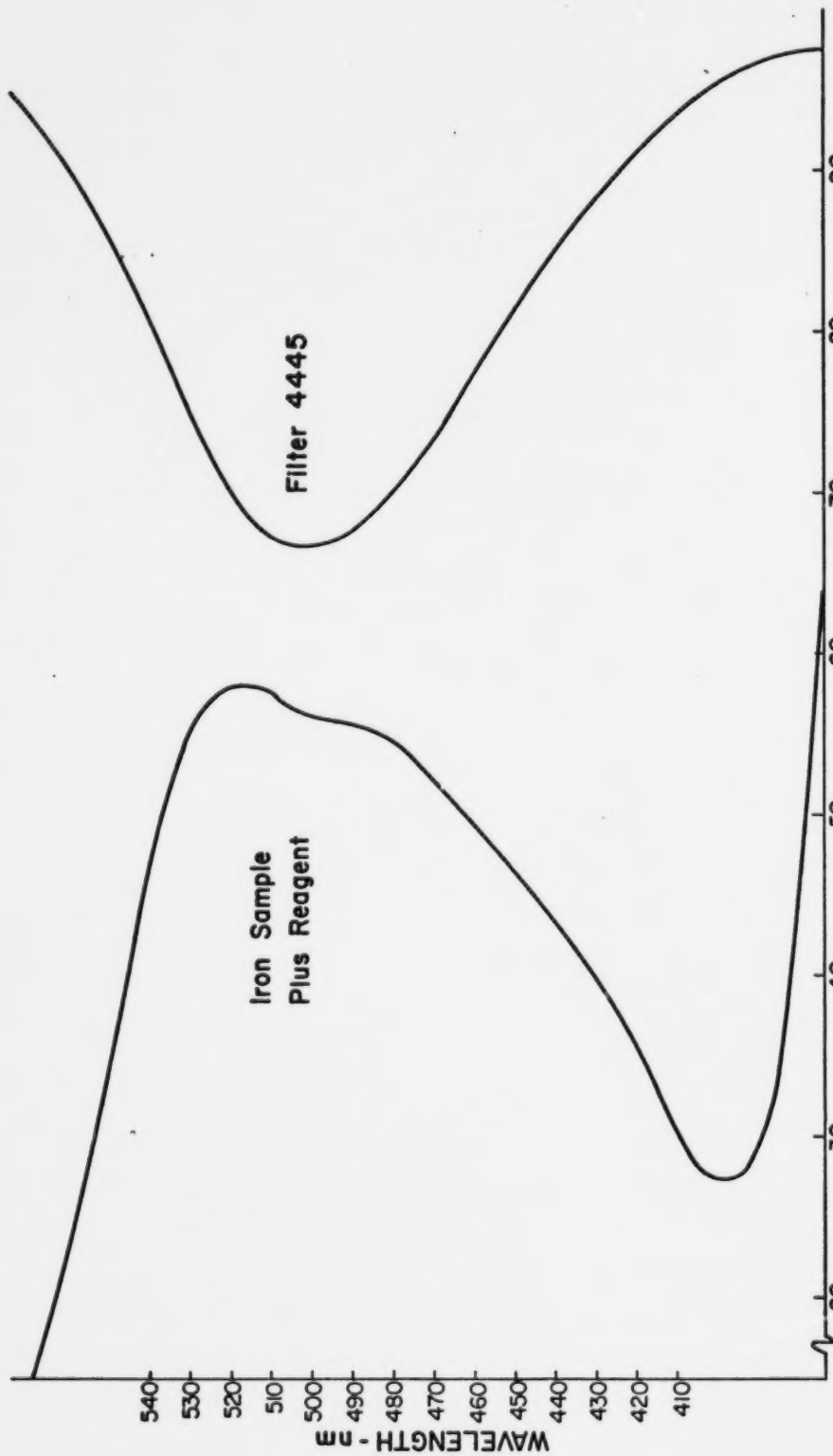

Figure 13. IRON ABSORBANCE SPECTRUM

MANGANESE TEST

The manganese test is colorimetric. Sodium periodate combines with manganese to form a pink color.

Standards

A stock solution containing 8 mg/l Mn was prepared by dissolving 24.6 mg $MnSO_4 \cdot H_2O$ in distilled water and diluting to 1.0 liter. Successive dilutions were made to obtain the following concentrations.

1	1 mg/l as Mn^{2+}
2	2 mg/l as Mn^{2+}
3	4 mg/l as Mn^{2+}
4	8 mg/l as Mn^{2+}

Calibrations

10 ml pipet	5 replicates	9.953 ± 0.0098 ml

Conclusions

Variation between replicates was less than 0.45 mg/l. This precision is approximately 10 percent at mid-range on the D-R scale and is acceptable for field use and most routine laboratory analyses.

It is recommended that the technician calibrate or verify calibration of the D-R scale with standard solutions. The D-R scale for this test, when adjusted to a standard solution in the range of expected use should provide acceptable accuracy. If not, the technician should prepare his own calibration chart using the transmittance scale and standard solutions.

It is difficult to dissolve the powder reagents by swirling as recommended by Hach. The solution must be shaken vigorously to obtain dissolution in a reasonable period of time.

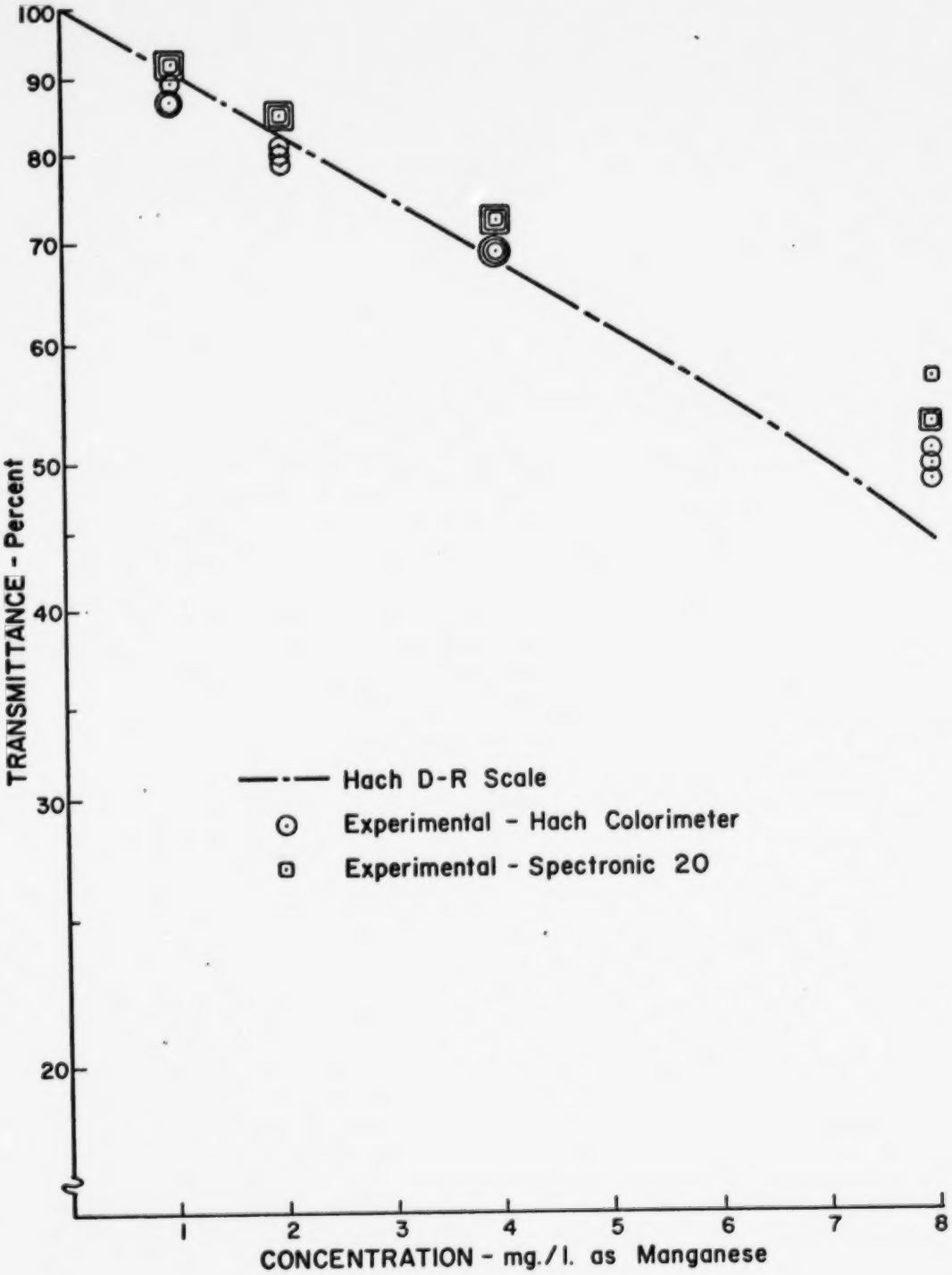

Figure 14. MANGANESE TEST

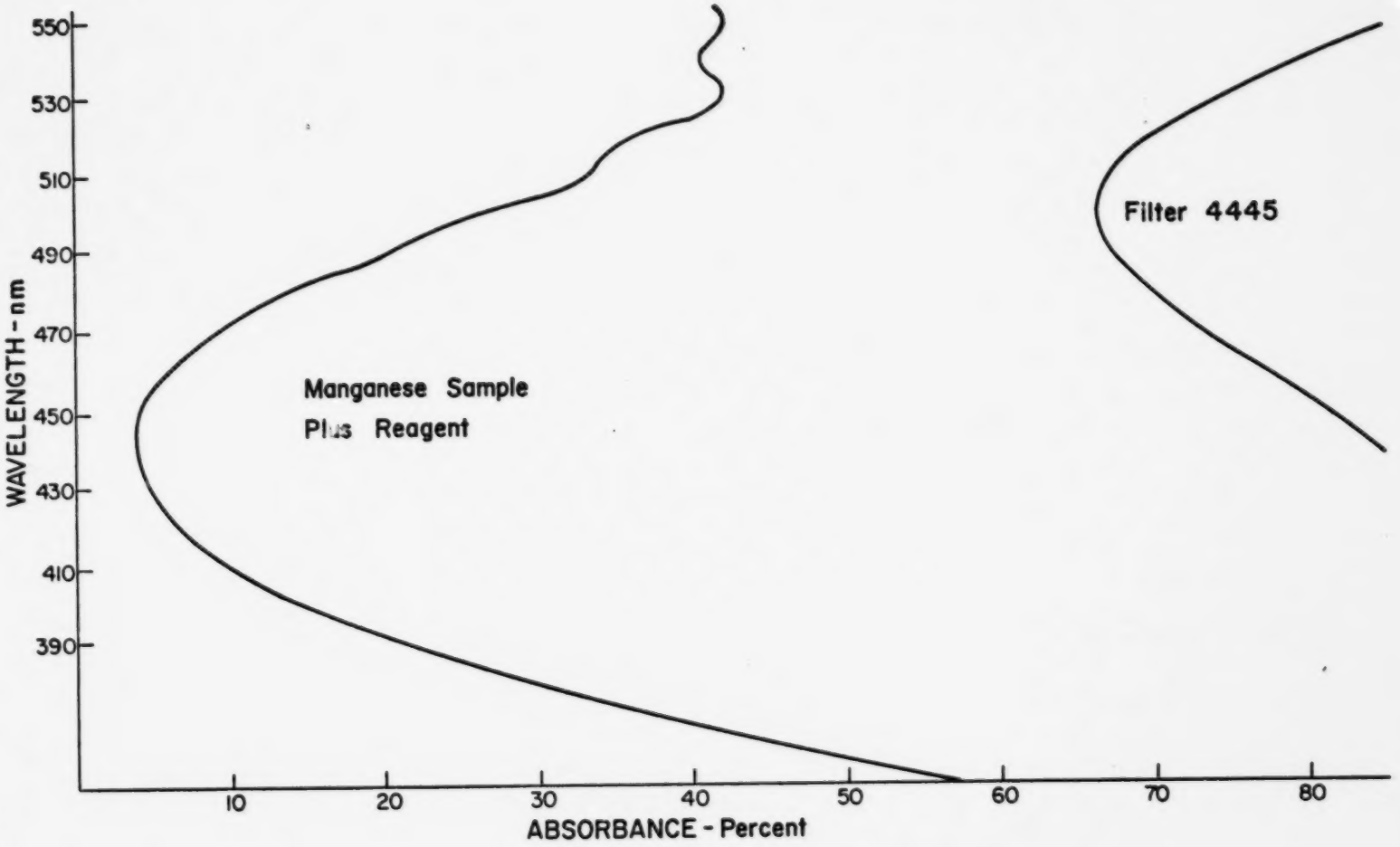

Figure 15. MANGANESE ABSORBANCE SPECTRUM

NITRATE TEST

The nitrate test is colorimetric. Cadmium reduction of nitrate to nitrite is followed by the color formation of diazotized sulfanilic acid and 1 - naphthylamine. A pink color is formed.

Standards

A stock solution containing 60 mg/l as N was made by dissolving 364.2 mg $NaNO_3$ in distilled water and diluting to 1.0 liter. Successive dilutions were made to give the following concentrations.

1	10 mg/l as N
2	20 mg/l as N
3	40 mg/l as N
4	60 mg/l as N

Calibrations

10 ml pipet	5 replicates	9.953 $\pm$ 0.009 ml

Conclusions

Maximum variation between replicates was 4 mg/l at 40 mg/l concentration. This represents a precision of 10 percent and is acceptable for field use and most routine laboratory analyses.

It is recommended that the technician calibrate or verify calibration of the D-R scale with standard solutions. The D-R scale for this test, when adjusted to a standard in the range of expected use should provide acceptable accuracy. If not, the technician should prepare his own calibration chart using the transmittance scale and standard solutions.

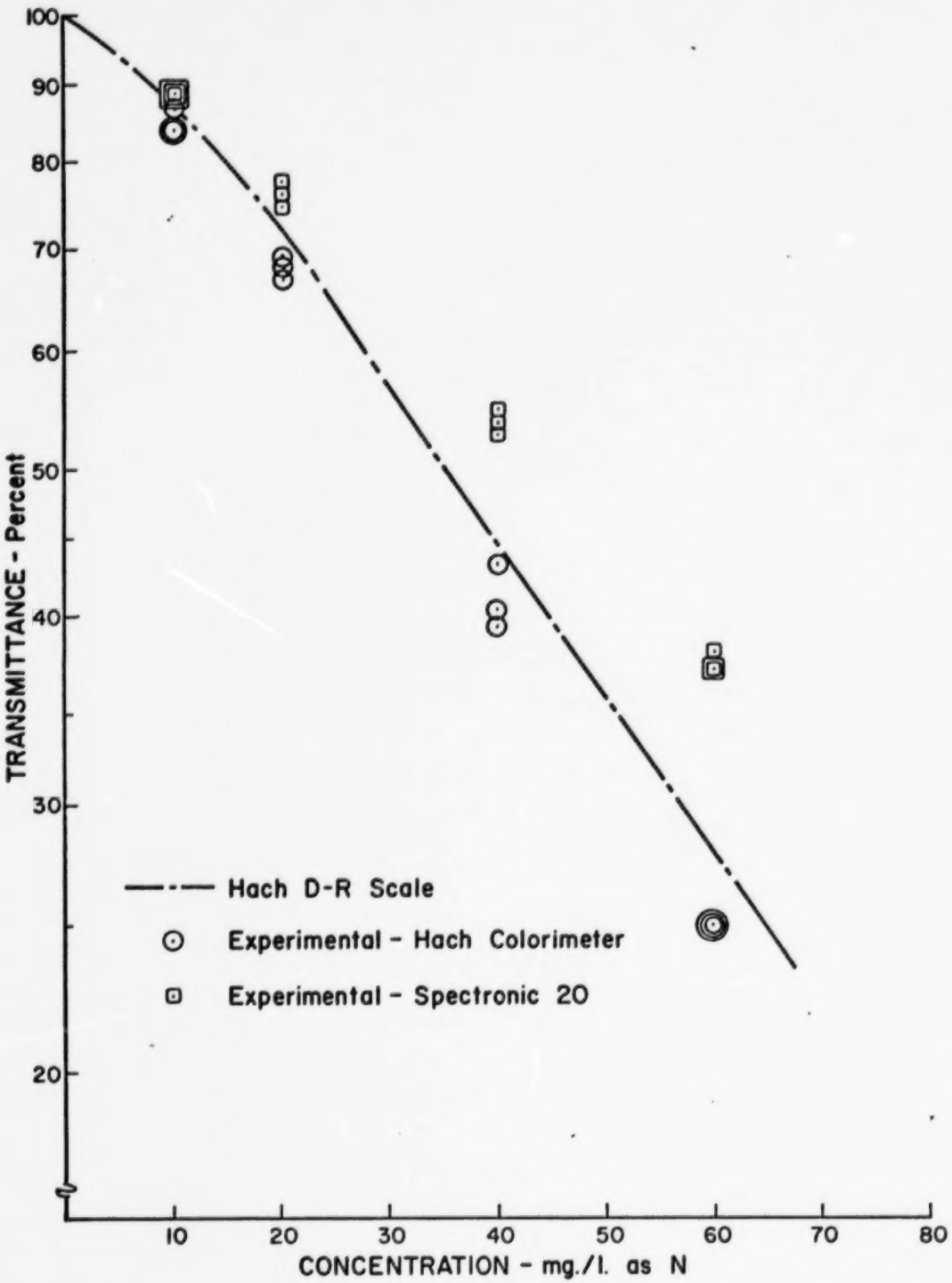

Figure 16. NITRATE TEST

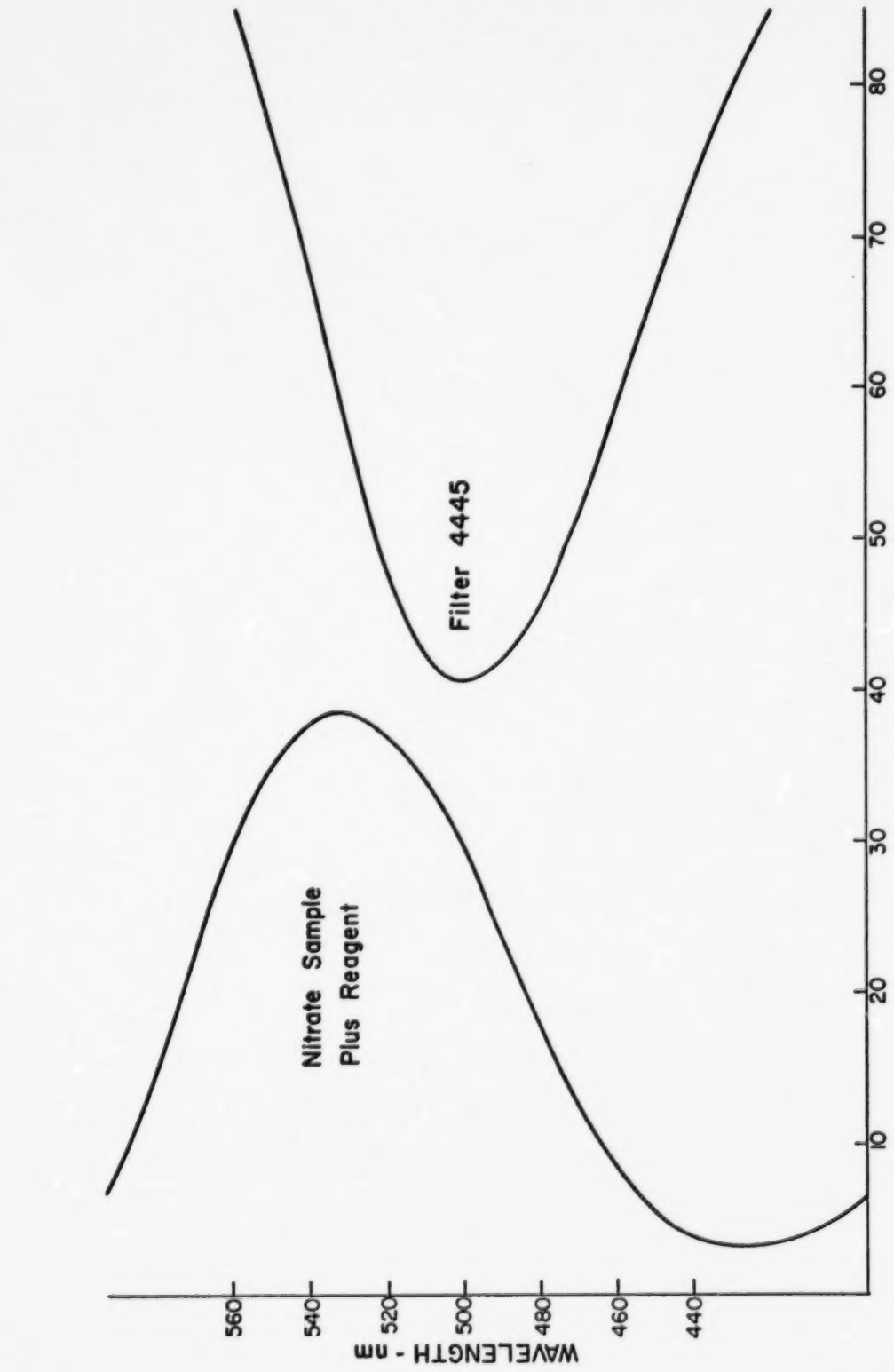

Figure 17. NITRATE ABSORBANCE SPECTRUM

NITRITE TEST

The nitrite test is colorimteric. A reddish purple azo dye is produced at pH 2.0 to 2.5 by the coupling of diazotized sulfanilic acid with naphthylamine hydrochloride.

Standards

A stock solution containing 1 mg/l concentration as N was prepared by dissolving 4.9 mg $NaNO_2$ in distilled water and diluting to 1.0 liter. Successive dilutions were then made to give the following standards.

1	.05 mg/l as N
2	.10 mg/l as N
3	.15 mg/l as N

Calibrations

10 ml pipet	5 replicates	9.953 ± 0.0098 ml

Conclusions

Maximum variation between replicates was .007 mg/l at .05 mg/l concentration. This represents a midrange precision of approximately 8 percent. This is acceptable for field work and most routine laboratory analyses.

It is recommended that the technician calibrate or verify calibration of the D-R scale with standard solutions. The D-R scale for this test, when adjusted to a standard in the range of expected use should provide acceptable accuracy. If not, the technician should prepare his own calibration chart using the transmittance scale and standard solutions.

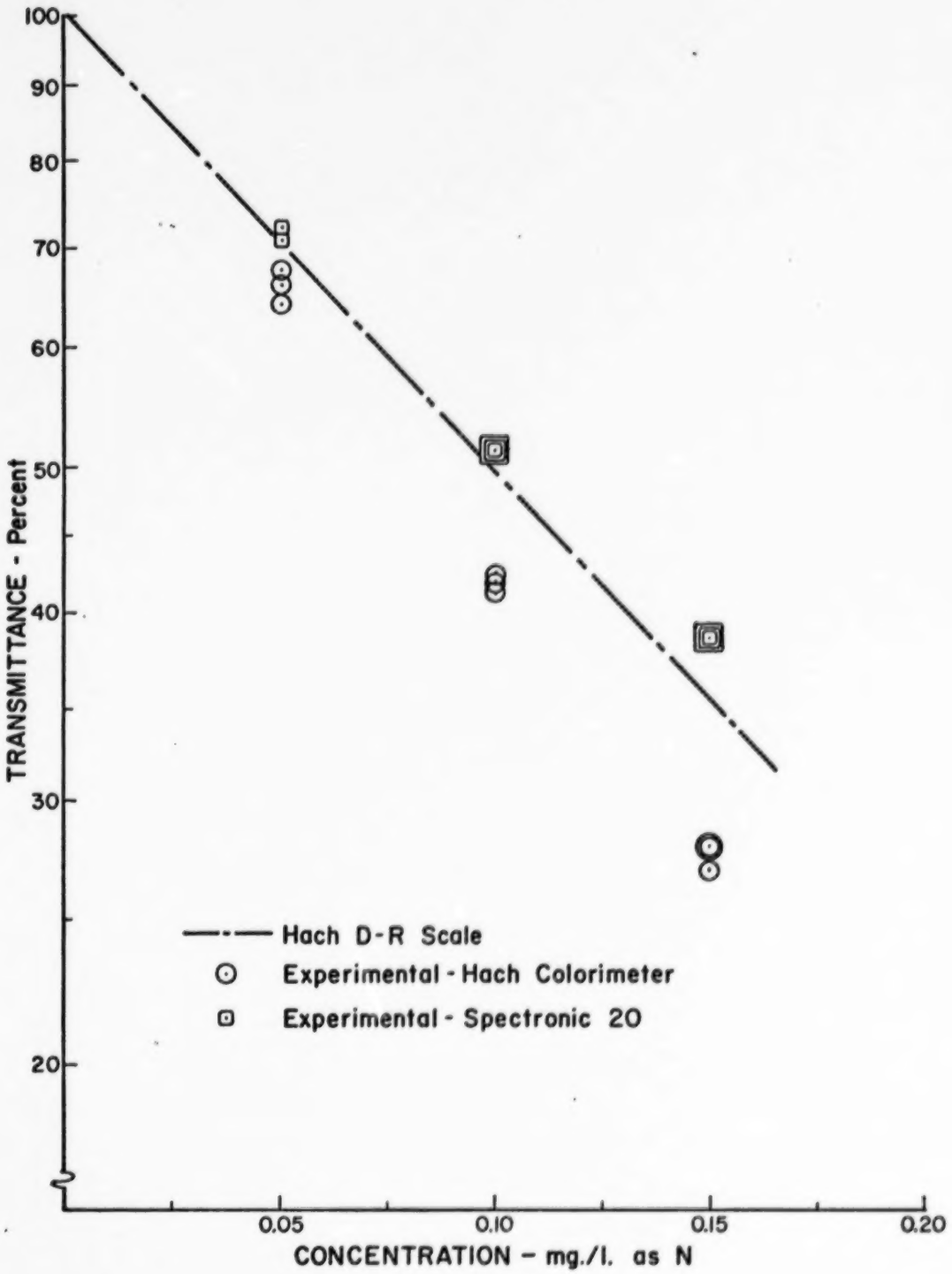

Figure 18. NITRITE TEST

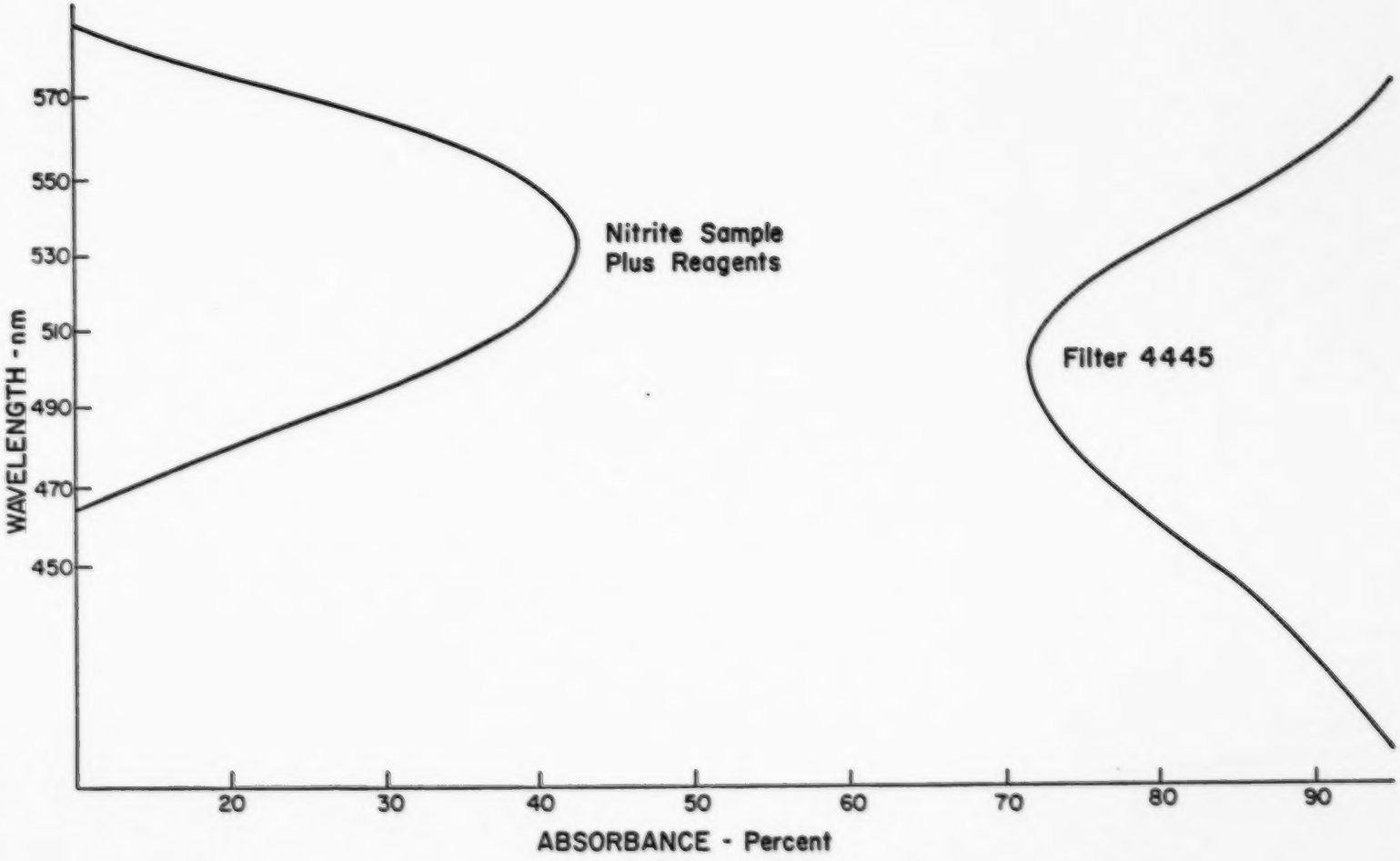

Figure 19. NITRITE ABSORBANCE SPECTRUM

OXYGEN (DISSOLVED) TEST

The dissolved oxygen test is titrimetric. It is essentially the Standard Winkler Method (Alsterberg Modification) with a new reagent, phenylarsene oxide (PAO), substituted for sodium thiosulfate. Manganese is used to reduce dissolved oxygen to a brown precipitate. Sulfamic acid converts the precipitated manganese to the Mn^{4+} form which will react with iodide ion I^-, to form I_2. The I_2 is titrated with PAO. The drop count titration technique (recommended by Hach) is used until the solution turns from yellow to colorless.

Standards

A stock solution of 7.5 mg/l of dissolved oxygen was made by aerating 10 liters of tap water for 24 hours. It was analyzed using the 200 ml sample and procedure for the Standard Winkler Method (Alsterberg Modification). The following standards were made by diluting the stock solution with unaerated tap water.

1	7.5 mg/l D.O.
2	6.4 mg/l D.O.
3	4.6 mg/l D.O.
4	3.9 mg/l D.O.
5	1.2 mg/l D.O.

Calibrations

D.O. dropper	16 $\pm$ 1 drops per ml
Standardized titer	0.01025 N PAO

Conclusions

Variation between replicates was approximately 1.0 mg/l at both high and low concentration. Use of the sampling tube as suggested will allow D.O. to be determined to the nearest whole mg/l since one drop = 1 mg/l. This variation is acceptable for field use. If greater precision is required, use two or four of the measuring tubes full of water rather than one only. The results would then be one drop = 1/2 mg/l and one drop = 1/4 mg/l respectively.

The dropper must be held vertically to insure uniform drop size.

The D.O. test is extremely reliable, even for an inexperienced technician.

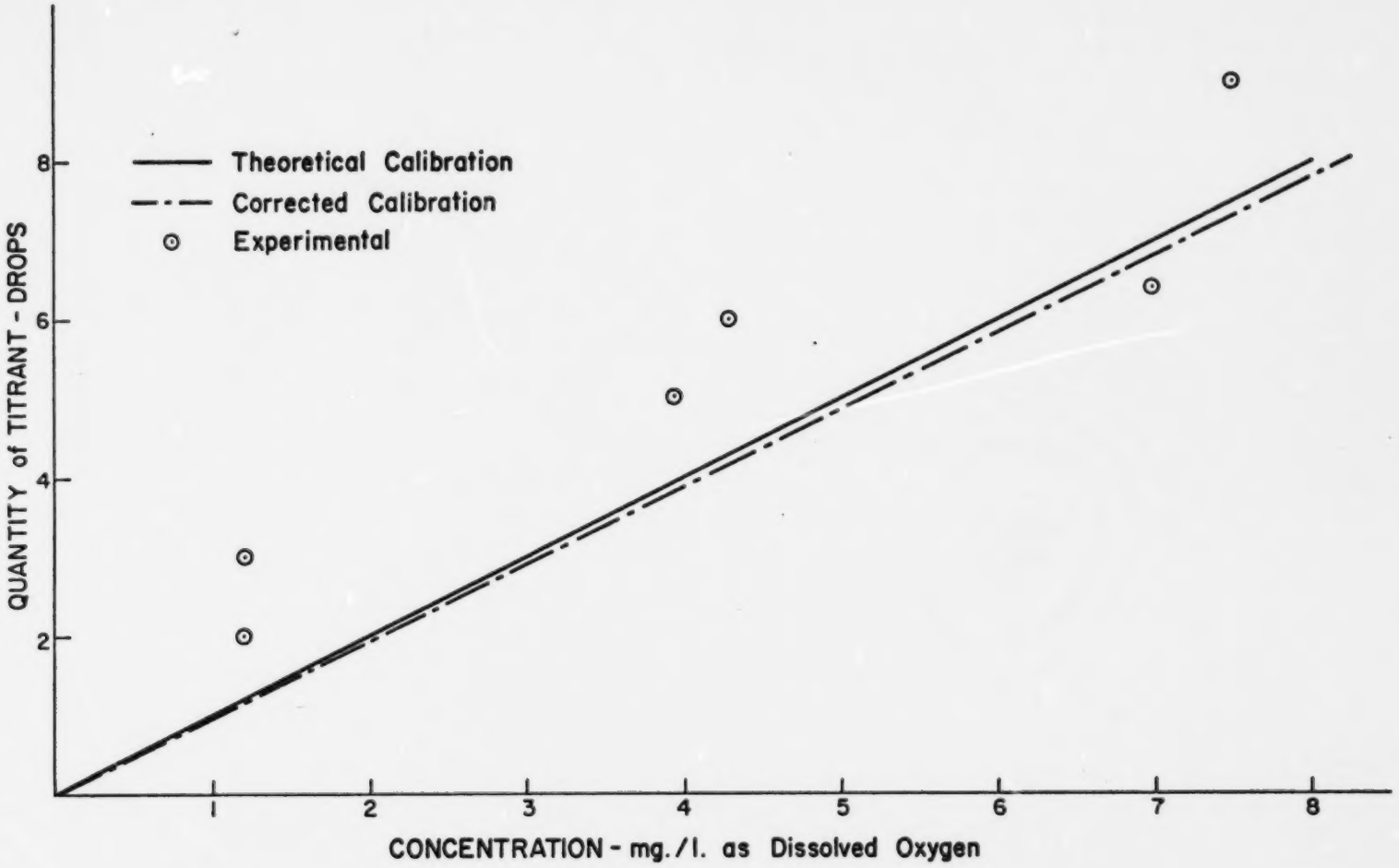

Figure 20. DISSOLVED OXYGEN (5.8 ml. sample)

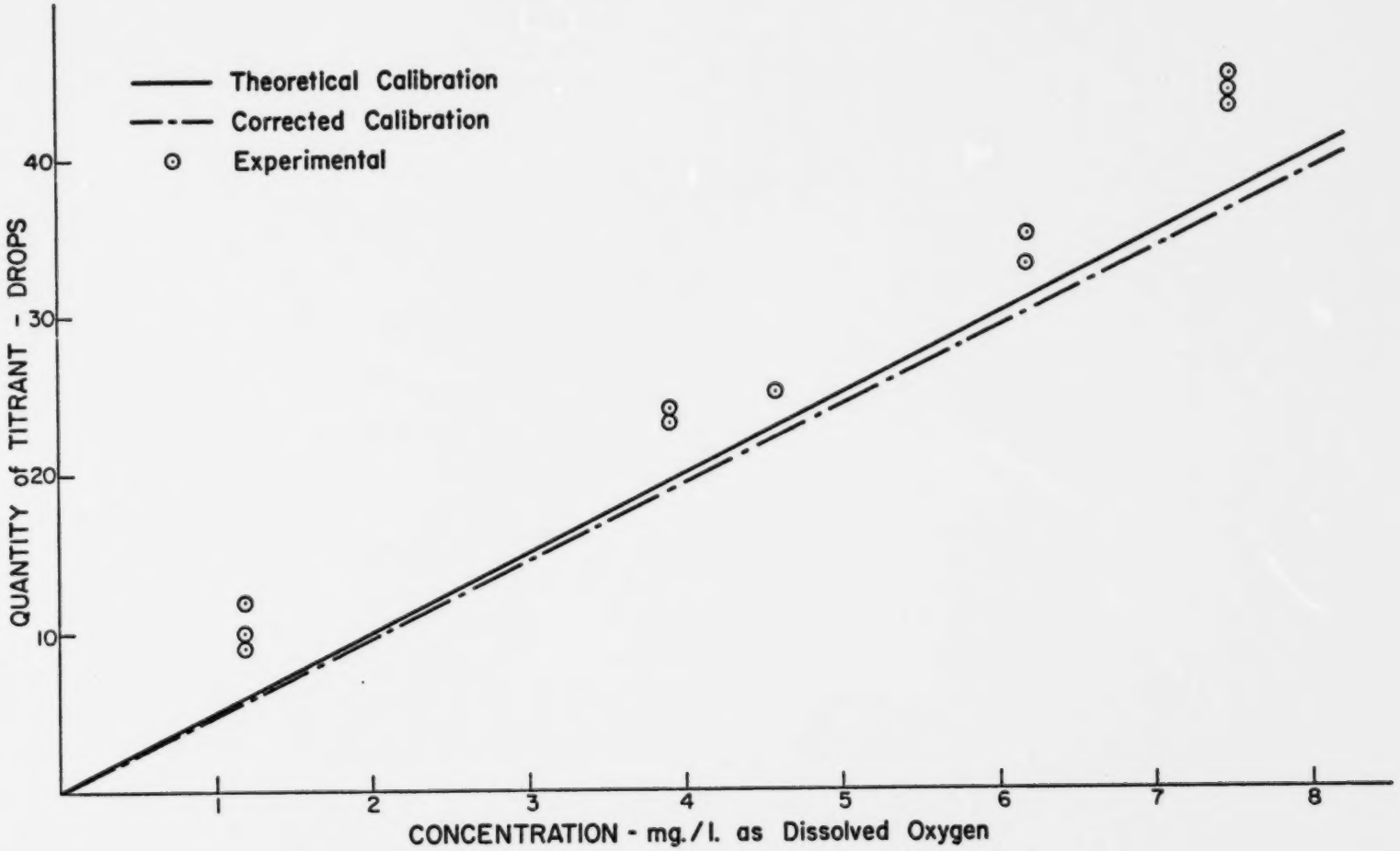

Figure 21. DISSOLVED OXYGEN (29 ml. sample)

pH TEST

The pH test utilizes a mixture of color indicators, each specific for a different pH. Either the colorimeter or visual comparison with a set of prepared standards is satisfactory.

Standards

Standards were made by titrating a sodium carbonate solution with sulfuric acid. A Coleman Model 10 pH Meter was the standard. The pH meter was calibrated with certified buffer solutions.

1	pH 9.98
2	pH 8.95
3	pH 8.02 (certified buffer 8.02 $\pm$ 0.01 pH)
4	pH 7.03 (certified buffer 7.03 $\pm$ 0.01 pH)
5	pH 5.96
6	pH 5.09
7	pH 3.99 (certified buffer 4.00 $\pm$ 0.01 pH)

Calibrations

25 ml graduated cylinder	3 replicates	24.81 $\pm$ 0.136 ml
10 ml pipet	5 replicates	9.953 $\pm$ 0.0098 ml

Conclusions

Variation between replicates was less than 0.2 pH units. This is excellent precision for colorimetric pH determination.

To eliminate meter drift, the buffer solution was used to set the colorimeter rather than a sample of distilled water. It was necessary to shake the wide range color indicator and the standards to achieve complete mixing.

It is recommended that the technician calibrate his D-R scale against certified buffer solutions and a well calibrated pH meter.

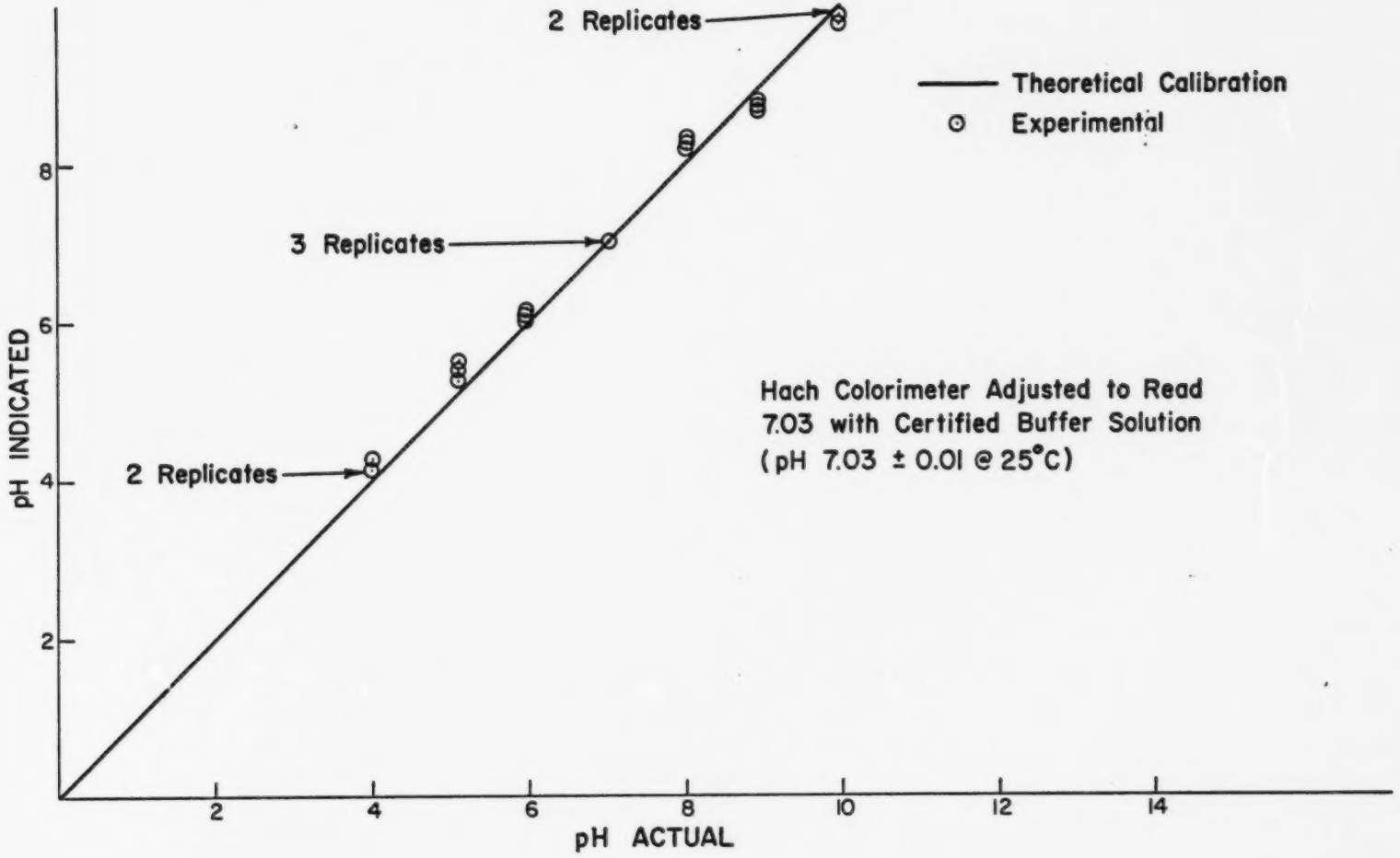
2 Replicates
Theoretical Calibration
Experimental
3 Replicates
2 Replicates
Hach Colorimeter Adjusted to Read
7.03 with Certified Buffer Solution
(pH 7.03 ± 0.01 @ 25°C)
pH INDICATED
pH ACTUAL
2
4
6
8
10
12
14

Figure 22. pH

PHOSPHATE, ORTHO TEST

The orthophosphate test is colorimetric. Ammonium molybdate and strong acid react with phosphate to form a light yellow color. A reducing agent for either the high or low concentration test will produce a more intense blue color.

Standards

A stock solution of 1000 mg/l as PO_4^{3-} was made by dissolving 1.435 g of KH_2PO_4 in distilled water and diluting to 1.0 liter. A second stock solution, 100 mg/l as PO_4^{3-}, was made diluting 100 ml of the first stock to 1.0 liter. The following standards were made by diluting the second stock solution.

1	0.2 mg/l as PO_4^{3-}
2	0.4 mg/l as PO_4^{3-}
3	0.8 mg/l as PO_4^{3-}
4	1.6 mg/l as PO_4^{3-}
5	1.0 mg/l as PO_4^{3-}
6	2.0 mg/l as PO_4^{3-}
7	3.0 mg/l as PO_4^{3-}
8	4.0 mg/l as PO_4^{3-}

Calibrations

Graduated cylinder	3 replicates	24.81 ± 0.134 ml

Conclusions

Variation between replicates is less than 0.4 mg/l at high range concentrations and is less than 0.2 mg/l in the low range. Greater precision would be desirable. It should be noted that the precision and accuracy of

this test are extremely dependent on careful control of time and temperature. Considerable practice is necessary to do a good job with this test.

The DR scale for the phosphate test is calibrated in terms of the PO_4^{3-} species even though a negligible portion of total phosphorous concentration is actually present at PO_4^{3-}. It is suggested that the DR scale furnished should be calibrated in terms of P.

It is recommended that the technician calibrate or verify calibration of the DR scale with standard solutions. The DR scale for this test, when adjusted to a standard in the range of expected use should provide acceptable accuracy. If not, the technician should prepare his own calibration chart using the transmittance scale and standard solutions.

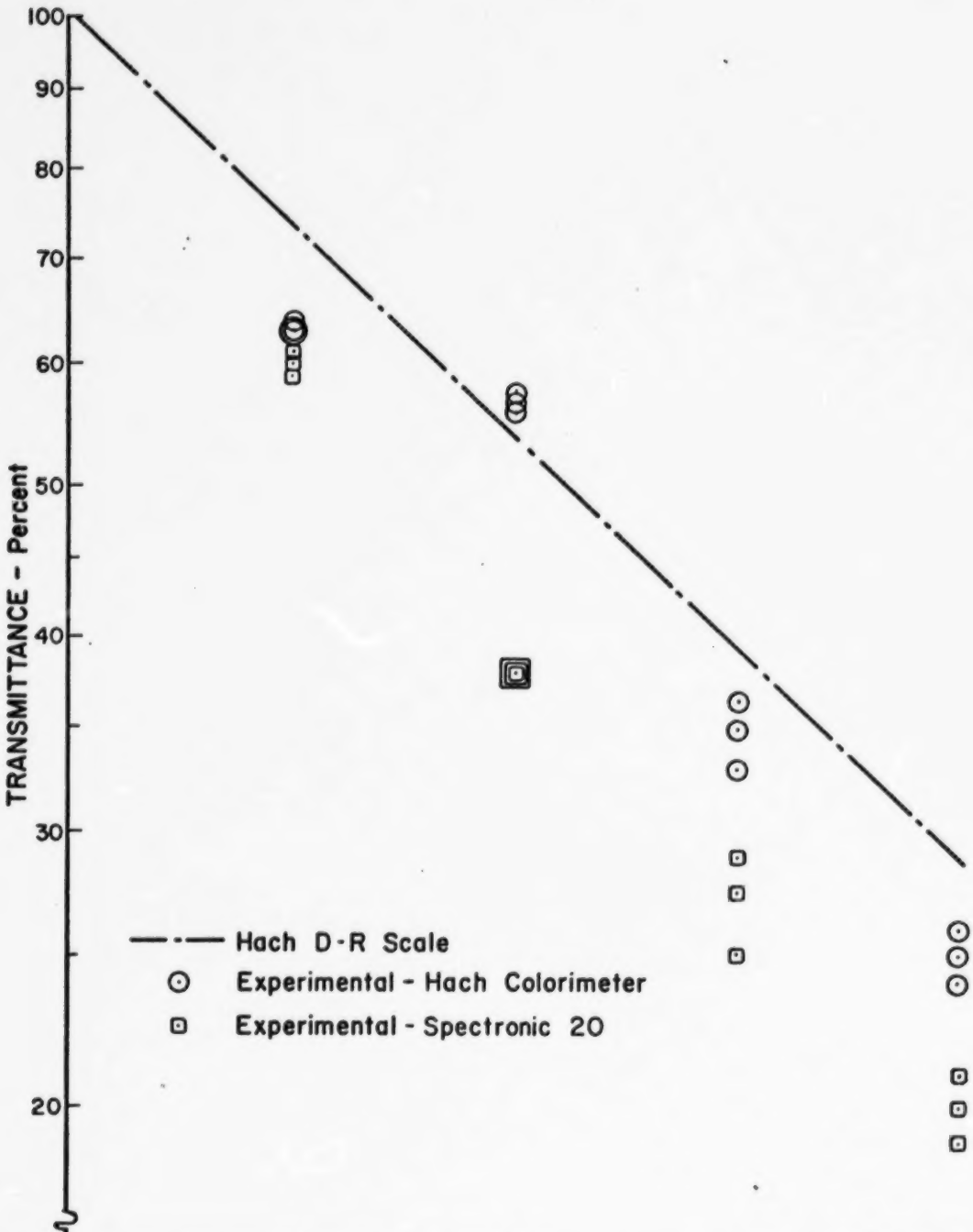

Figure 23. PHOSPHATE, ORTHO - HIGH RANGE

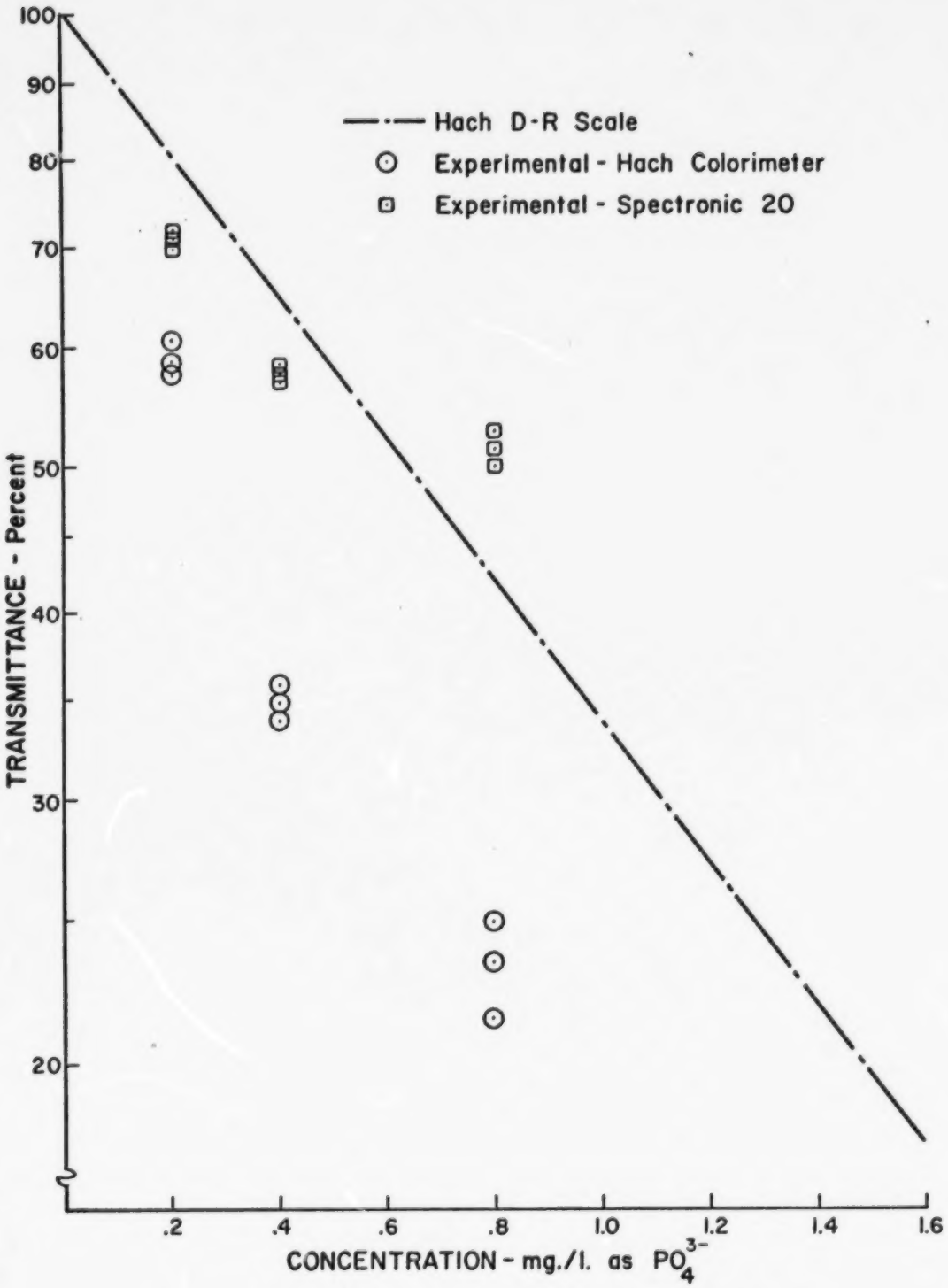

Figure 24. PHOSPHATE, ORTHO - LOW RANGE

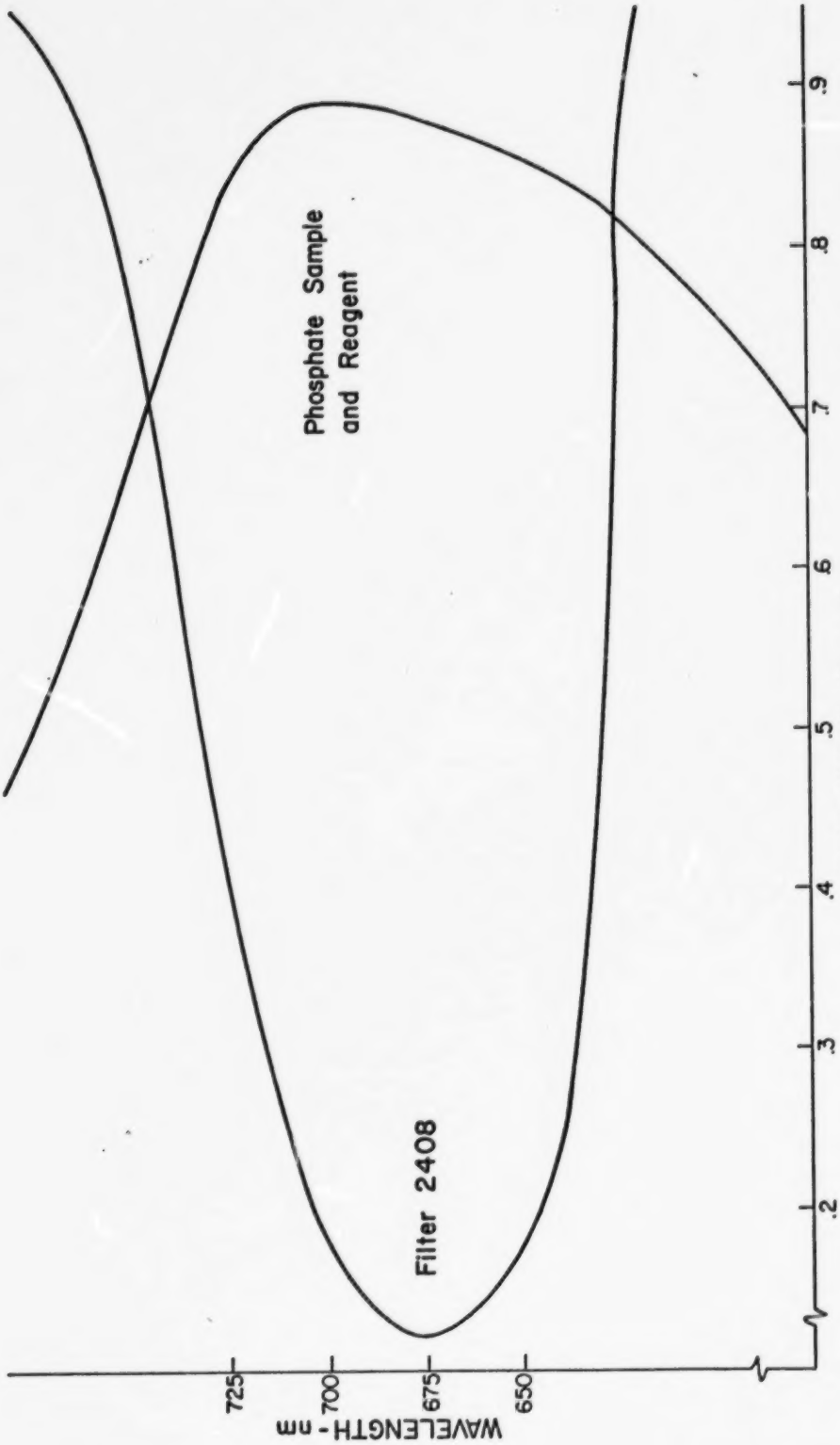

Figure 25. PHOSPHATE ABSORBANCE SPECTRUM

PHOSPHATE, TOTAL, TEST

The total phosphate test is colorimetric. Metaphosphate is converted into orthophosphate by digesting. The test for total phosphate is identical to the test for orthophosphate. Metaphosphate is found by subtracting orthophosphate from total phosphate.

Standards

A stock solution of 400 mg/l as metaphosphate was made by dissolving 0.430 g of sodium metaphosphate, $(NaPO_3)_6$ in distilled water and diluting to 1.0 liter. A second stock solution, 100 mg/l as metaphosphate was made by diluting 250 ml of the first stock to 1.0 liter.

The following standards were made by diluting the stock solution.

1	8 mg/l as PO_4^{3-}
2	4 mg/l as PO_4^{3-}
3	2 mg/l as PO_4^{3-}
4	1 mg/l as PO_4^{3-}

Calibrations

Graduate cylinder	3 replicates	24.81 ± 0.134 ml

Conclusions

Variation between replicates at high total phosphate concentrations is less than 0.3 mg/l, and is less than 0.1 mg/l for low phosphate concentrations. This test is the same as the orthophosphate test but the precision is much improved. The investigators obviously gained experience between this test and the orthophosphate test. Practice is recommended for all of the phosphate analyses.

The test showed a more complete change of polymeric phosphates to PO_4^{3-} when a hot plate was used instead of the Sterno burner. The points obtained using the hot plate seem to be closer to the direct readout graph. For reliability this test should be performed under laboratory conditions, and not in the field.

The DR scale for the phosphate test is calibrated in terms of the PO_4^{3-} species even though a negligible portion of total phosphorous concentration is actually present as PO_4^{3-}. It is suggested that the DR scale furnished should be calibrated in terms of P.

It is recommended that the technician calibrate or verify calibration of the DR scale with standard solutions. The DR scale for this test, when adjusted to a standard in the range of expected use should provide acceptable accuracy. If not, the technician should prepare his own calibration chart using the transmittance scale and standard solutions.

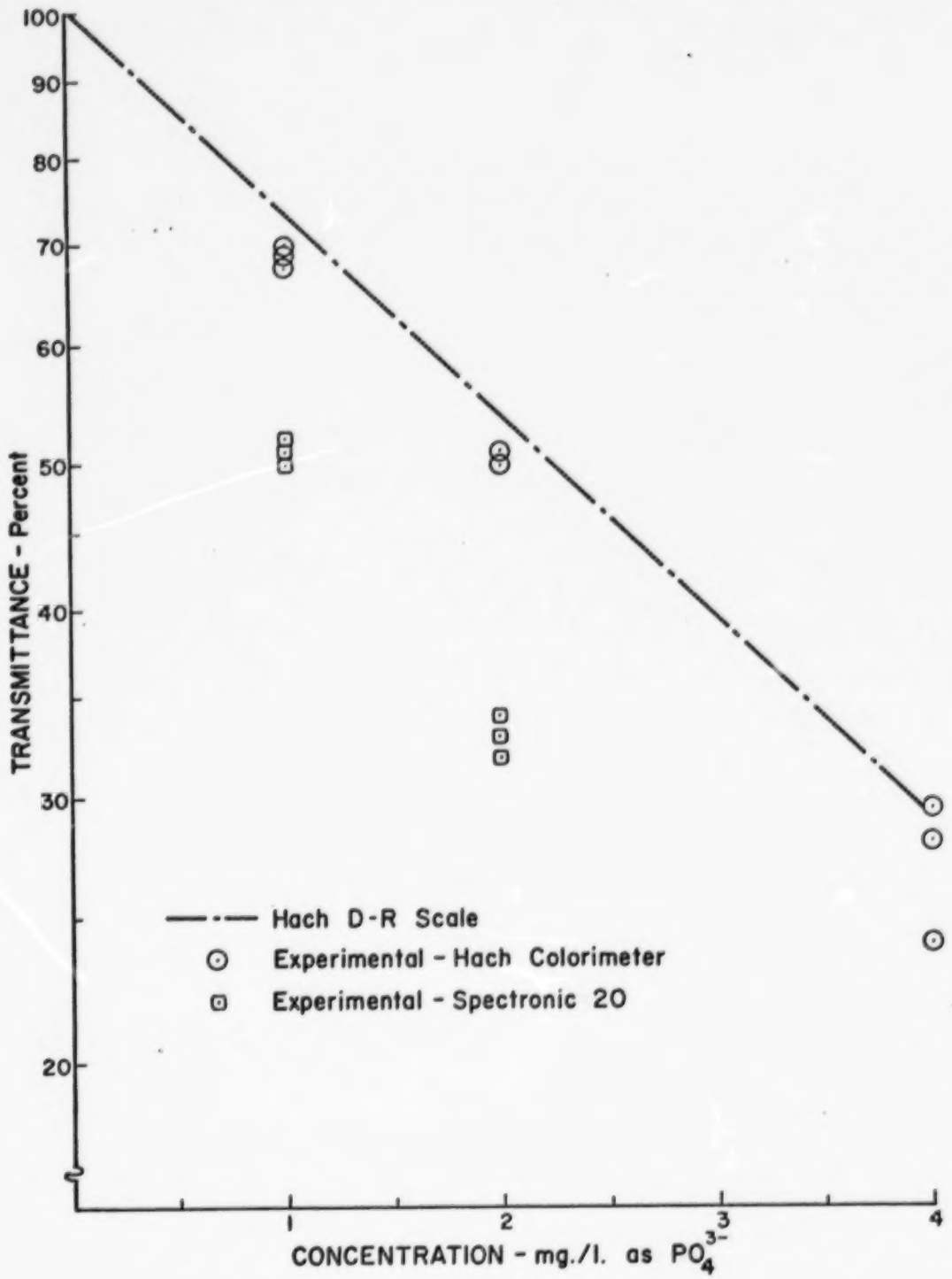

Figure 26. PHOSPHATE, TOTAL - HIGH RANGE

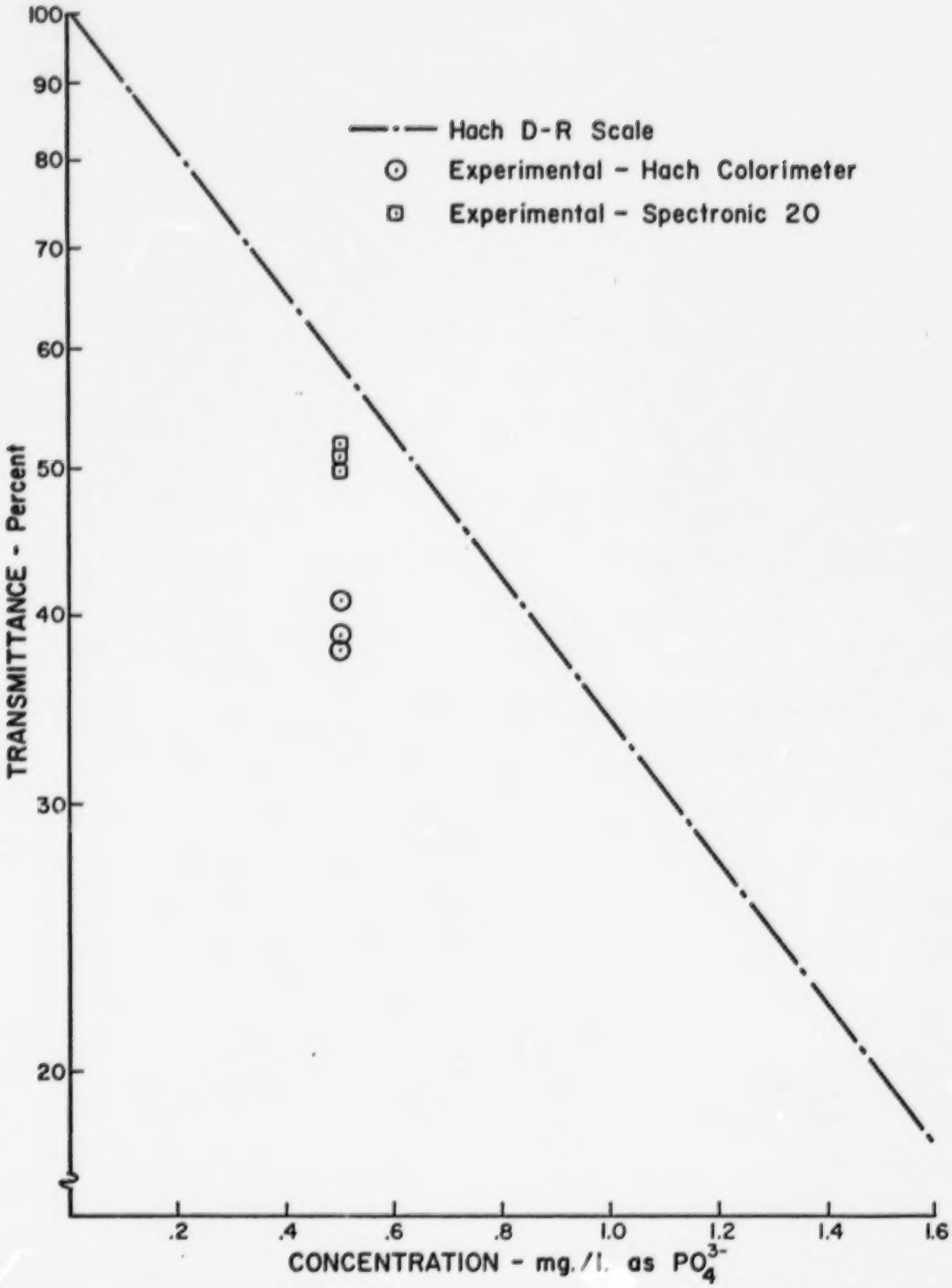

Figure 27. PHOSPHATE, TOTAL - LOW RANGE

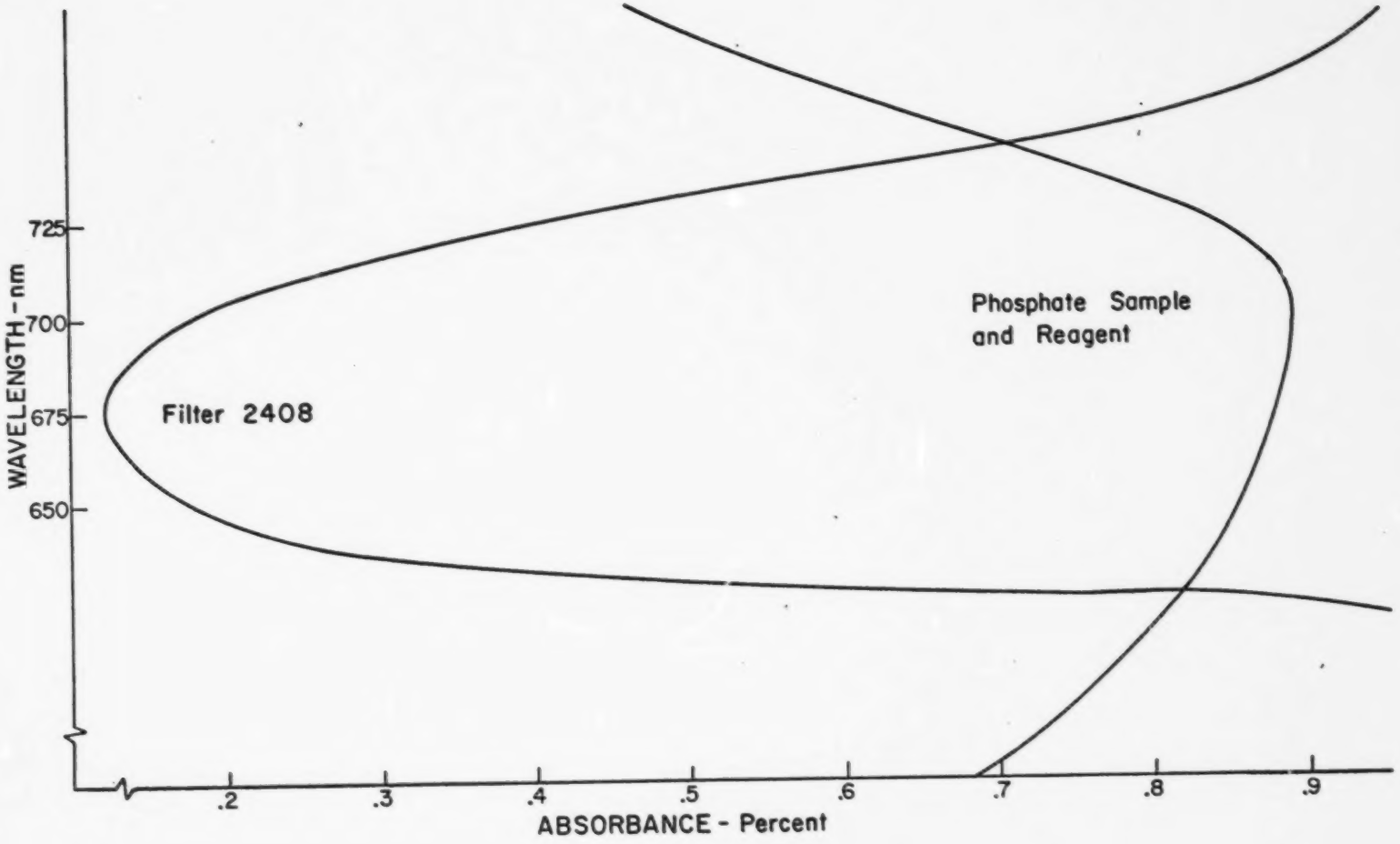

Figure 28. PHOSPHATE ABSORBANCE SPECTRUM

SILICA TEST

The silica test is colorimetric. Acid and molybdate react with silica to form a yellow color. For low concentrations of silica, the color is faint and amino acid is added to produce a relatively dark blue color.

Standards

A stock solution of 1000 mg/l as SiO_2 was made by dissolving 4.733 mg of sodium meta-silicate, $Na_2SiO_3 \cdot 9H_2O$ in distilled water and diluting to 1.0 liter. A second stock solution of 100 mg/l SiO_2 was made by diluting 100 ml of the first stock to 1.0 liter. The following standards were made by diluting the second stock solution.

1	0.5 mg/l as SiO_2
2	1.0 mg/l as SiO_2
3	1.5 mg/l as SiO_2
4	2.0 mg/l as SiO_2

Calibrations

25 ml graduated	3 replicates	24.81 ± 0.134 ml

Conclusions

Variation between replicates is less than 0.2 mg/l at SiO_2 concentrations of 2.0 mg/l and is less than 0.1 mg/l at SiO_2 concentrations of 0.5 mg/l. This precision is acceptable for field use and routine laboratory analyses.

The silica test is calibrated for SiO_2, even though the scale and the procedure have title: "Silica".

It is recommended that the technician calibrate or verify calibration

of the D-R scale with standard solutions. The D-R scale for this test, when adjusted to a standard in the range of expected use should provide acceptable accuracy. If not, the technician should prepare his own calibration chart using the transmittance scale and standard solutions.

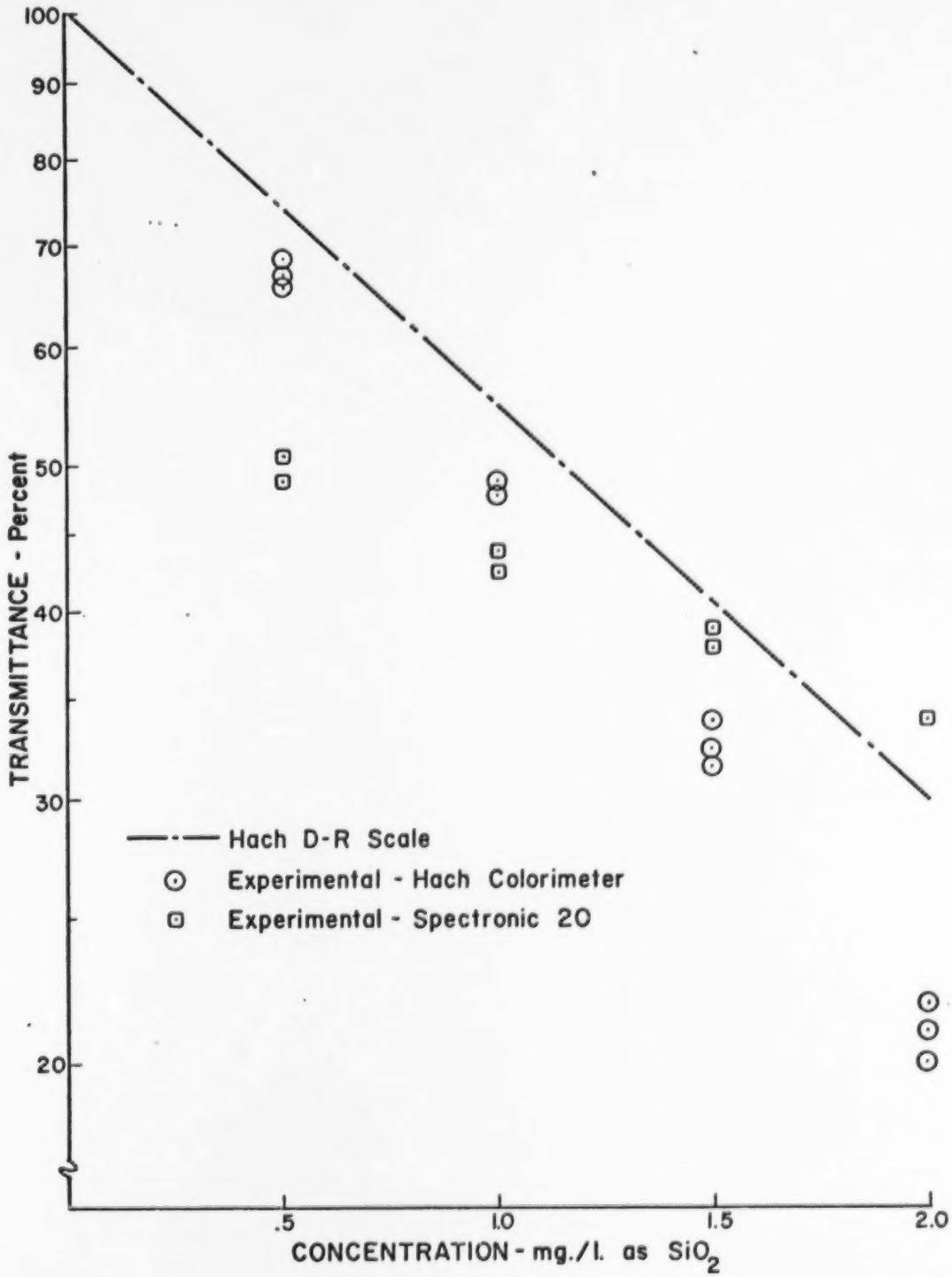

Figure 29. SILICA TEST

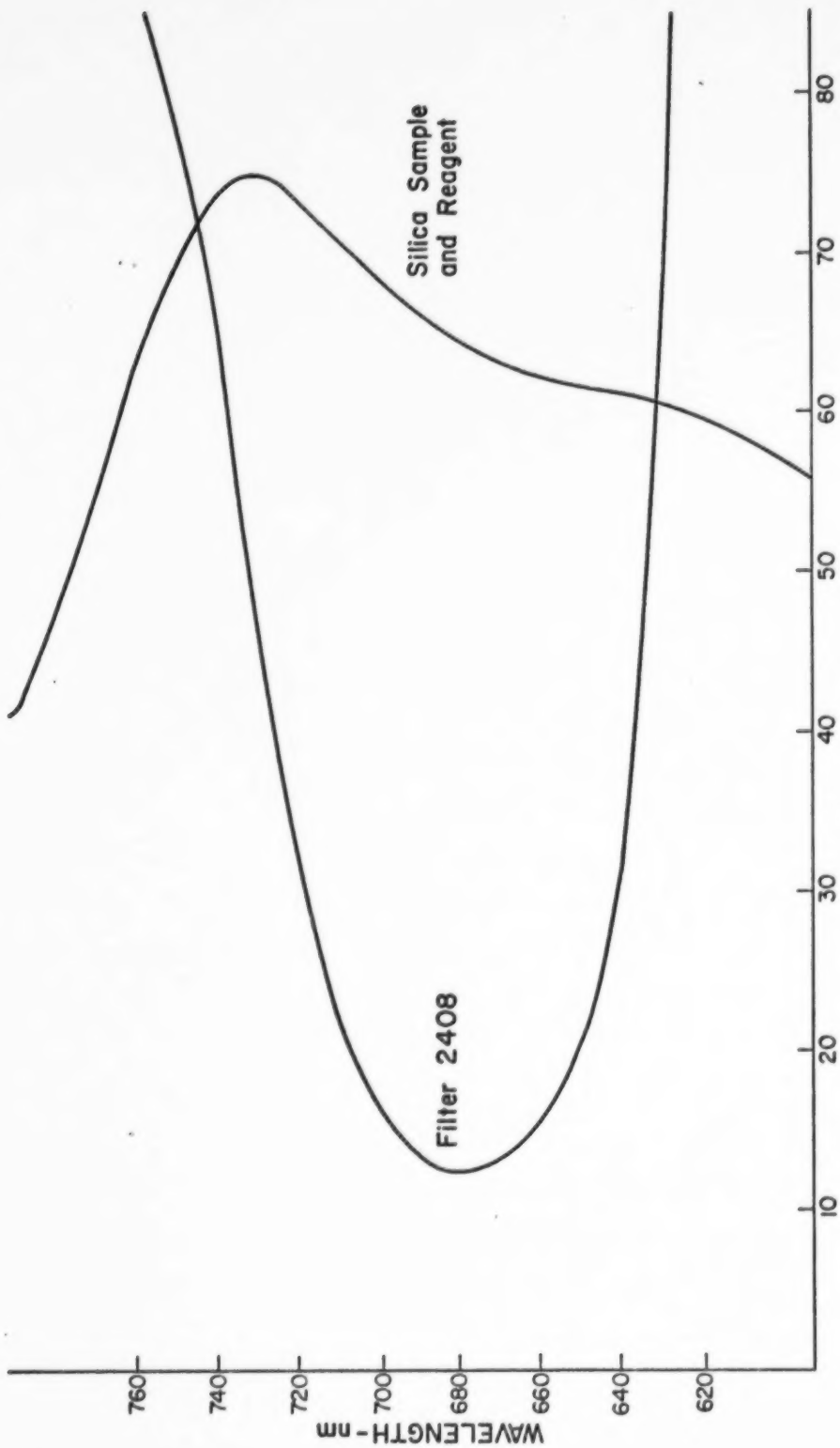

Figure 30. SILICA ABSORBANCE SPECTRUM

SULFATE TEST

The sulfate test is turbidimetric. A soluble barium salt reacts with sulfate to form the precipitate barium sulfate. The precipitate suspension is stabilized and measured for light scattering ability. Since Hach only provides a colorimeter, light penetration rather than scattering is measured.

Standards

A stock solution of 1000 mg/l as SO_4^{2-} was made by dissolving 1.480 grams of sodium sulfate, Na_2SO_4, in distilled water and diluting to 1.0 liter. The following standards were then made by diluting the stock solution

1	20 mg/l as SO_4^{2-}
2	40 mg/l as SO_4^{2-}
3	80 mg/l as SO_4^{2-}
4	160 mg/l as SO_4^{2-}

Calibration

25 ml graduated cylinder	3 replicates	24.81 ± 0.136 ml

Conclusions

Variations between replicates is approximately 15 percent. A turbidimetric analysis is difficult to perform on a colorimeter. Since the test is not colorimetric, Beer's Law is not followed. In fact filter selection is rather unimportant. For best results on the Hach colorimeter, the investigators recommend using the filter suggested by Hach, but the operator should prepare his own calibration chart, using the transmittance scale and standard solutions.

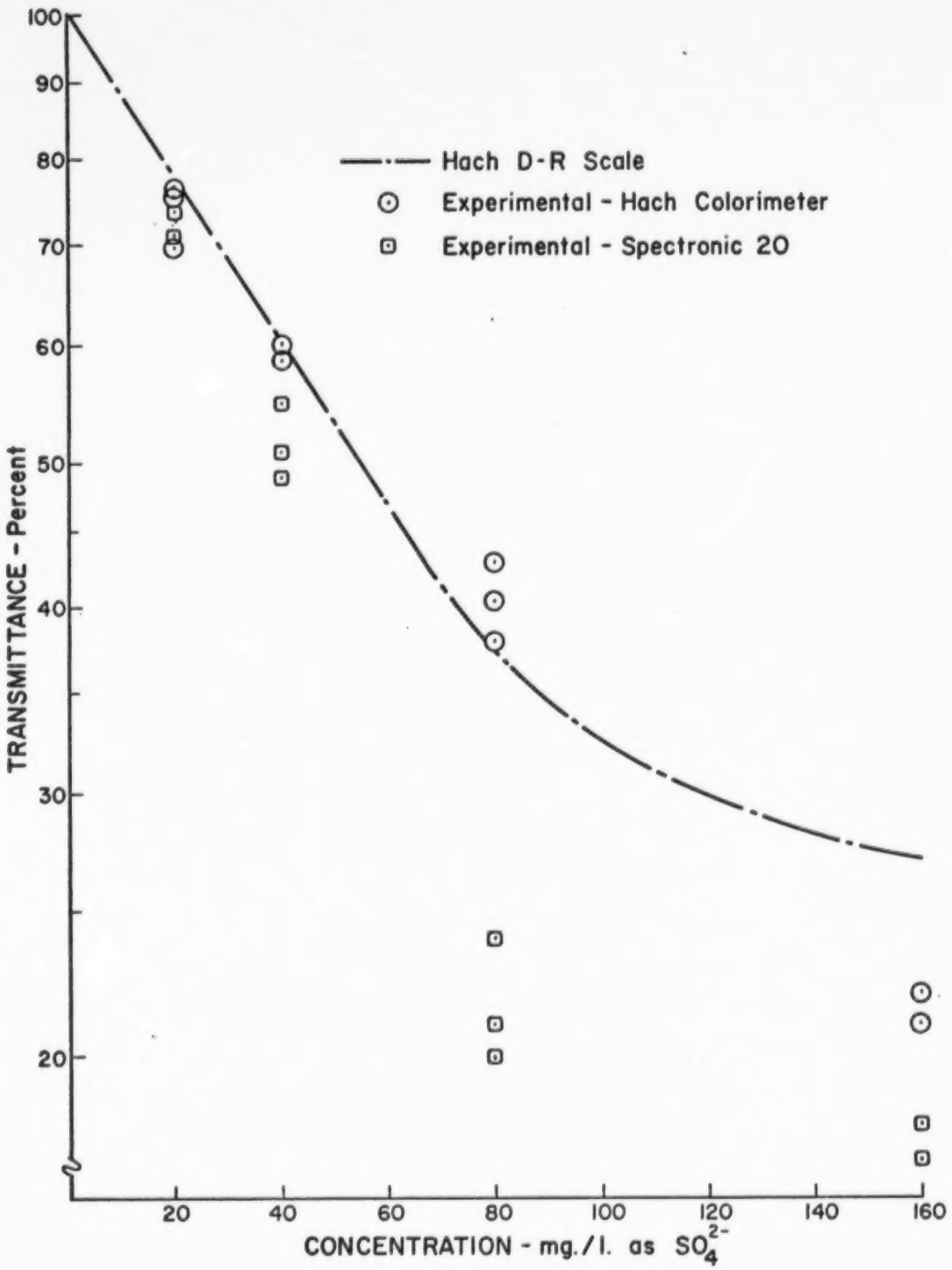

Figure 31. SULFATE TEST

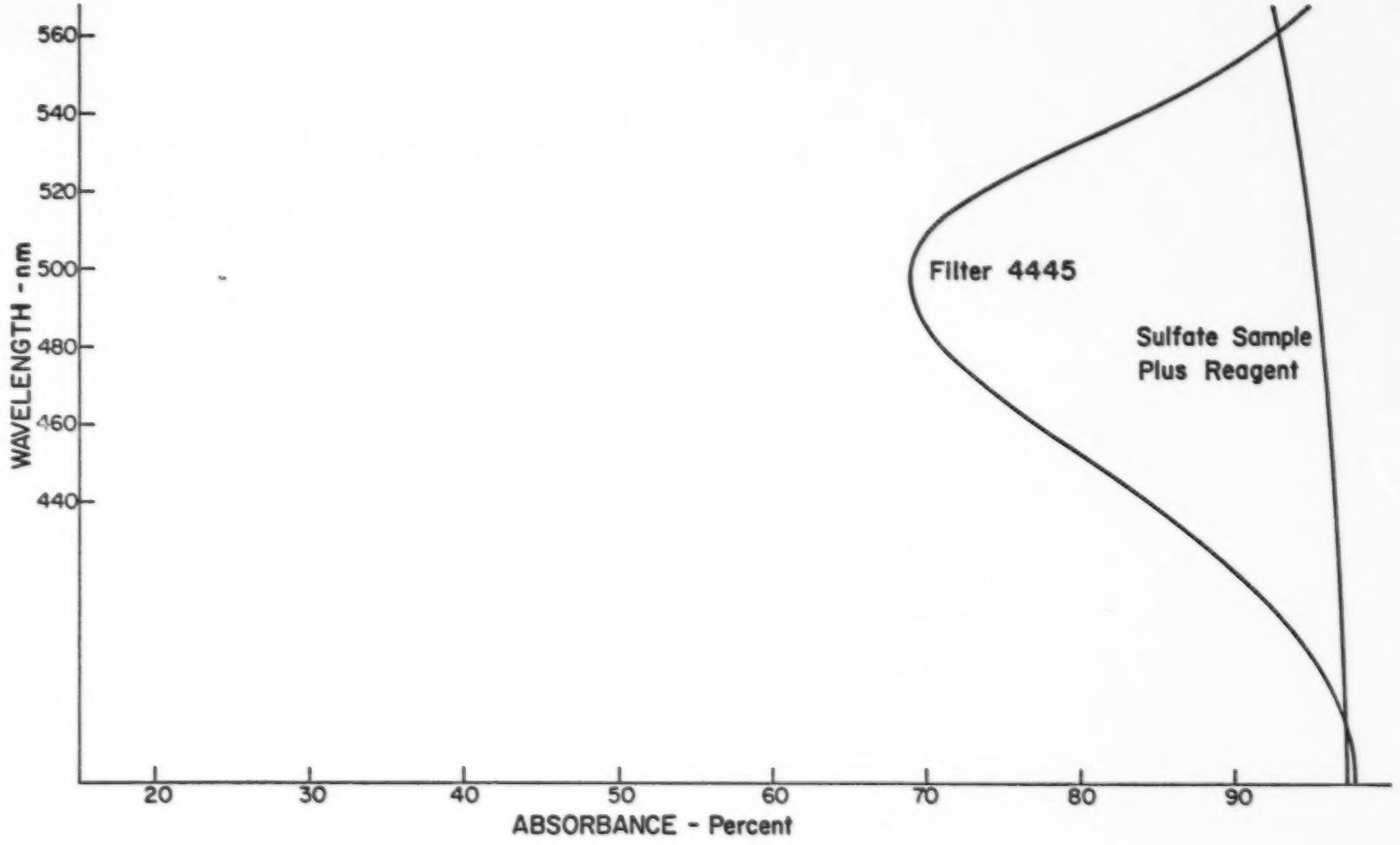

Figure 32. SULFATE ABSORBANCE SPECTRUM

TURBIDITY TEST

The turbidity test normally utilizes the principle of light scattering rather than light absorption. Since Hach only provides a colorimeter with the DR-EL unit, light penetration must be measured.

Standards

A stock solution of 950 JTU was made by dissolving approximately 40 grams of clay, in distilled water. Settleable matter was separated by decantation. The following standards were then made by diluting the stock solution and standardizing against a Jackson turbidimeter.

1	950 JTU
2	470 JTU
3	245 JTU
4	123 JTU
5	57 JTU

Recommended Standards (Hach)

A stock formazine suspension of 400 JTU is made as follows:

Solution A. Dissolve 1.00 g hydrazine sulfate in 100 ml distilled water.

Solution B. Dissolve 10.00 g hexamethylenetetramine in 100 ml distilled water.

Add 5 ml solution A to 5 ml solution B. Let stand for 24 hours at 25 $\pm$ 3° C. Dilute to 100 ml. The following standards are then made by diluting the stock solution with distilled water.

1	400 JTU
2	300 JTU
3	200 JTU
4	100 JTU
5	50 JTU

Calibrations

25 ml graduated cylinder	3 replicates	24.81 $\pm$ 0.136 ml

Conclusions

Variations between replicates is less than 40 JTU for any concentration between 0 and 500 JTU.

The formazin reference method with which the Hach colorimeter is calibrated would be expected to give more reproducible results than a random clay sample.

Turbidity is not a quantitative determination, but an optical phenomenon. As particle size, shape, color, and distribution vary, the light penetration and light scattering vary. It is recommended that the technician prepare his own calibration chart, using the transmittance scale and standards from the particular sample being determined.

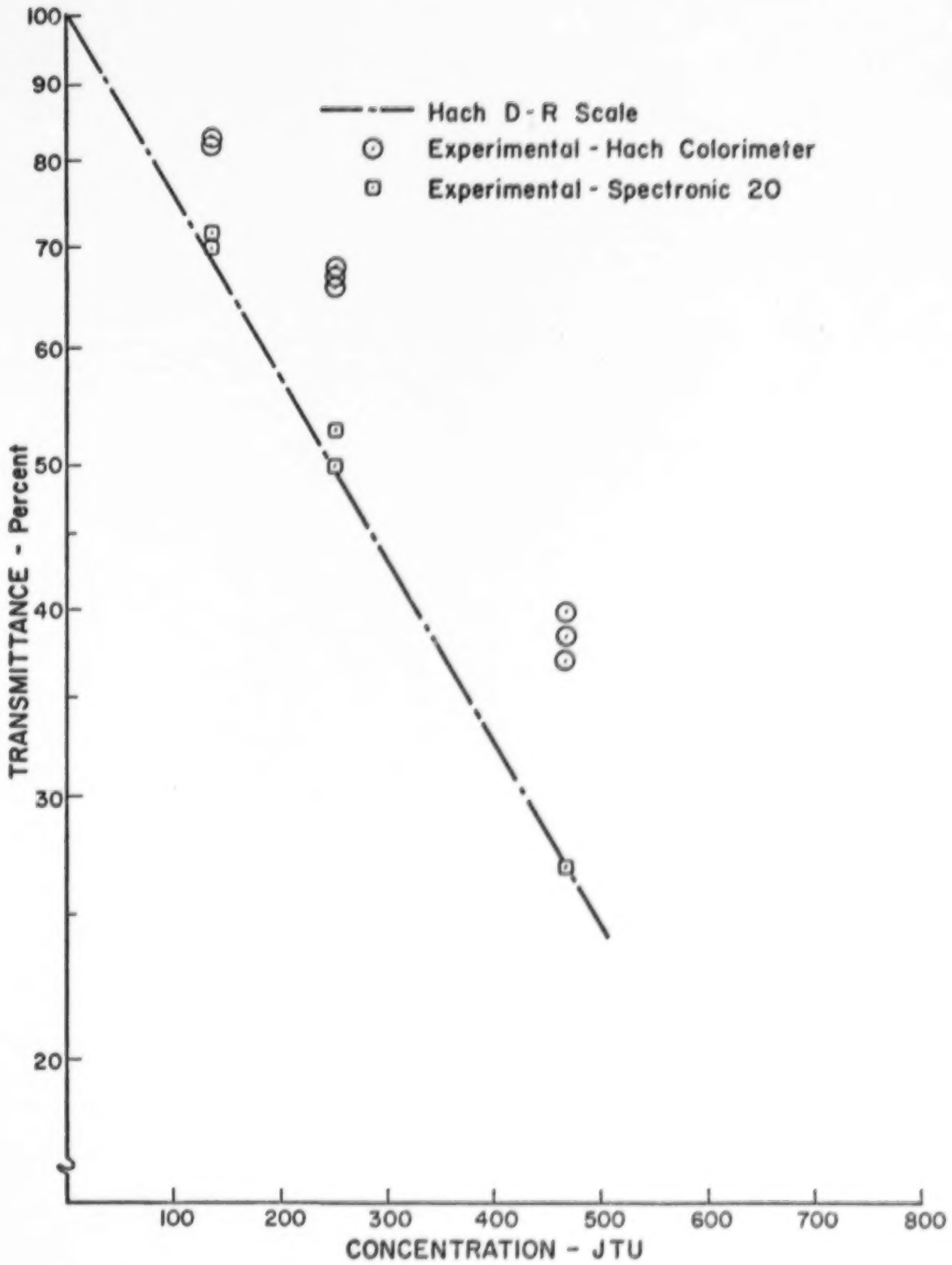

Figure 33. TURBIDITY TEST

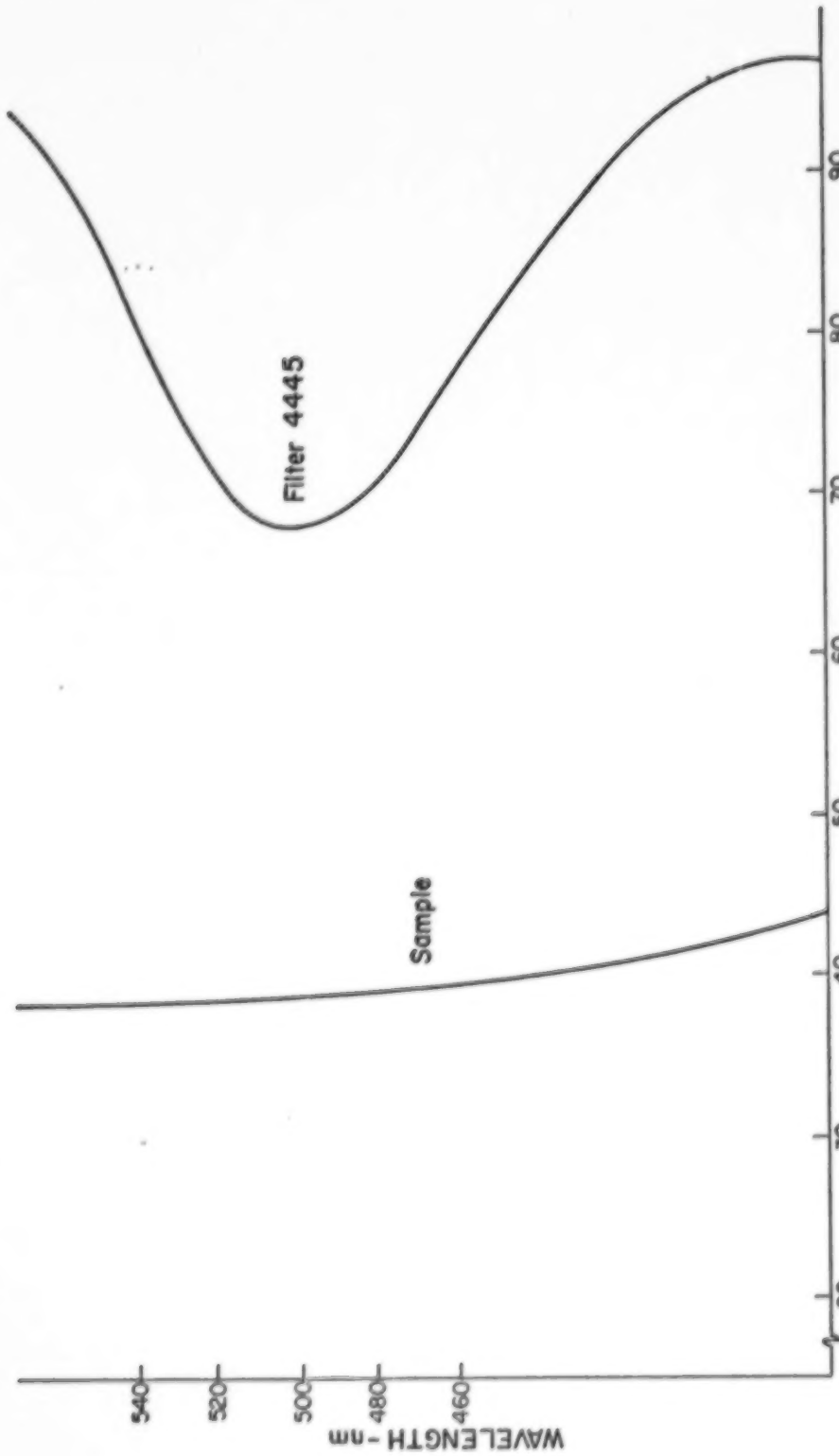

Figure 34. TURBIDITY ABSORBANCE SPECTRUM